

To the Graduate Council

I am submitting herewith a dissertation written by Eun Ju Moon entitled “Controlled self-organization and tunable collective phenomena in surface-based nanostructures.” I have examined the final copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy with a major in Physics.

Hanno H. Weitering, Major Professor

We have read this dissertation
And recommend its acceptance:

James R. Thompson

Zhenyu Zhang

David C. Joy

Accepted for the Council:

Carolyn R. Hodges

Vice Provost and Dean of the Graduate School

(Original signatures are on file with official student records)

**Controlled Self-organization and Tunable Collective
Phenomena
in Surface-based Nanostructures**

A Dissertation
Presented for the
Doctor of Philosophy
Degree
The University of Tennessee, Knoxville

Eun Ju Moon
December 2009

To my parents

Acknowledgments

Since this dissertation is the result of many individual efforts combined directly or indirectly, I would like to take this opportunity to express my sincere gratitude for all those who have guided and supported me through this work.

First and foremost, I gratefully thank my research advisor, Dr. Hanno H. Weitering, for his support and guidance throughout this research, and opening my eyes to new ideas in every step along the way. Thank you for patiently sharing your knowledge and teaching me how to present my scientific findings. You gave me all the freedom and support I needed to develop and realize my own ideas. I would also like to thank my dissertation committee; Drs. James R. Thompson, Zhenyu Zhang, and David C. Joy for their valuable suggestions and comments. Dr. Thompson, you are a constant source of inspiration; it was great to work with you. Thanks for your great collaboration in the study of superconductive properties of the ultrathin alloy films. I was also fortunate to discuss several aspects of this work with Dr. Zhang. I appreciate the discussions, advice, and help I received from him. I wish to thank all members and collaborators of Dr. Zhenyu Zhang's group. Collaborations with Dr. Fernando Flores and Dr. Jose Ortega at Universidad Autónoma, Madrid in Spain have enriched my research on the discrete distribution of one dimensional lattice model and have led to a good publication. I also wish to thank Dr. Jia Yu at Zhengzhou University in China, for his expert support with DFT calculations of the film thickness dependent surface. I extend my thanks to Dr. Adolfo G. Eguiluz for his collaboration with plasmon modes in ultrathin metal films. I want to thank Randy McMillan for his technical support. I also would like to thank Dr. Norman Mannella for his assistance with scientific and technical questions regarding X-ray Photoelectron Spectroscopy.

My thanks are also extended to everybody in Dr. Hanno Weitering's group; Saban Hus, Violeta Iancu, Mustafa M. Özer, Changgan Zeng, Jiangdong Guo, and many others for their support and helpful discussions. I thank Mustafa M. Özer for his expert help with the SQUID magnetometer measurements and for his collaboration with the Mg Plasmons in ultrathin films

included in this dissertation. Grateful acknowledgement is extended to Dr. Geun Seop Lee, for advice and interesting discussions.

Wonderful friends in Knoxville have made these years at UTK much more enjoyable. I would like to thank Valentina Kuznetsova, Minghu Pan, Hong Liu, and in particular Suzanne Parete-Koon, Paul Snijders, Teyu Chen, and many others for their friendship. Many thanks also to Juan Pablo Urrego-Blanco for his invaluable friendship and the endless conversations we had. My life has been richer and more joyful in past years having best friends Mi Jin Noh and Nasrin Mirsaleh-Kohan on my side. Thank you for your support and love.

Finally, I would like to thank my parents Kyu Hyeon Moon and Jeong le Kim, my sisters Eun Young and Eun Mi, and my brother Jeong Yeol for their care and support across the distance and throughout the years. Thank you for your understanding and love as I explore the world. You always believed in me, and made possible my physics studies.

“ . . .

*The wind is rising! . . . We must try to live!
The huge air opens and shuts my book: the wave
Dares to explode out of the rocks in reeking
Spray. Fly away, my sun-bewildered pages!
Break, waves! Break up with your rejoicing surges
This quiet roof where sails like doves were pecking.
(Translated by C. Day Lewis)*

*Le vent se lève! . . . il faut tenter de vivre!
L'air immense ouvre et referme mon livre,
La vague en poudre ose jaillir des rocs!
Envolez-vous, pages tout éblouies!
Rompez, vagues! Rompez d'eaux rejouies
Ce toit tranquille où picoraient des focs
”*

Le cimetière marin by Paul Valéry

Abstract

Nanostructure systems possessing certain desirable features can arise from the self-organization of fundamental building blocks. In this thesis we explore two types of *controlled* self-assembly mechanisms in hetero-epitaxy: (a) classical assembly of atom vacancies into quasi one-dimensional line structures and (b) quantum-driven assembly of atoms into atomically-smooth two-dimensional thin films. In the classical assembly phenomenon, adatom vacancies, created via elastic strain-relaxation in compressively strained atom chains on a silicon substrate, self-organize into meandering vacancy lines. The average spacing between these line defects can be varied by adjusting the chemical potential μ of the adsorbed atoms. We implemented a lattice model that quantitatively connects density functional theory calculations for perfectly ordered structures to the fluctuating disorder seen in experiment and the experimental control parameter μ . The quantum-mechanical thin-film assembly explored in this thesis has an electronic origin. It is made possible by strong quantum size effects at the nanoscale and can be controlled experimentally by tuning the quantum mechanical boundary conditions and free carrier density of an ultrathin metal film. This is accomplished via atomic-scale template modification and chemical doping, respectively. Our investigations focused on the formation and structure-property relationship of these engineered quantum films, and specifically on the emergence of collective phenomena such as superconductivity and plasmon excitations. We succeeded in growing atomically-smooth $\text{Pb}_{1-x}\text{Ga}_x$ ($x = 0.06$) alloy films on a $\text{Si}(111)\text{-}7 \times 7$ substrate through quantum confinement, a remarkable observation because Pb and Ga are totally immiscible in the bulk. The resulting films exhibit large uniform-depth holes which turn out to be responsible for the exceptionally large critical current density in these films. Remarkably, the critical current density *increases* with temperature up to 3.25 K, a phenomenon that has not been seen before and that can be attributed to the unusual quantum-growth morphology of this material. The alloying experiments furthermore elucidate the likely origin of the T_c suppression generally observed in thin films. Finally, we demonstrate the existence of quantized plasmon modes in ultrathin metal

films. Controlled self-organization experiments thus enable stabilization of novel nanophase materials, which in turn leads to discovery and understanding of novel collective properties.

Contents

1. INTRODUCTION	1
1.1. Self-organizing systems	2
1.2. Self-assembly formations in hetero-epitaxy	3
1.2.1. Self-assembly of atom vacancies	3
1.2.2. Self-assembly of atoms in classical film growth	4
1.2.3. Self-assembly of atoms in quantum growth	5
1.3. Experimental Control	8
1.3.1. Template modification	8
1.3.2. Chemical doping	9
1.4. Scope and overview of the thesis	9
2. SURFACE SCIENCE METHODS AND BACKGROUND	14
2.1. X-ray Photoelectron Spectroscopy (XPS)	15
2.1.1. Theoretical Background	15
2.1.2. XPS applications	17
2.2. Low Energy Electron Diffraction (LEED)	20
2.2.1. Theoretical Background	20
2.2.2. LEED applications	23
2.3. Scanning Tunneling Microscopy (STM)	23
2.4. Superconducting QUantum Interference Device magnetometer (SQUID)	26
2.5. Interface Reconstruction	28
2.5.1. Si(111)- 7×7 surface	28
2.5.2. Si(111)- $\sqrt{3} \times \sqrt{3}$ R30°-(M) surface	30
2.5.3. “Devil’s staircase” ($1.2 < \theta < 1.3$ ML)	31
3. CONTROLLED SELF-ORGANIZATION OF ATOM VACANCIES IN MONATOMIC GALLIUM LAYER	35
3.1. Introduction	36
3.2. Experimental Procedures	38
3.3. Results and Discussions	38
3.4. Summary	45

4. QUANTUM STABILITY AND SUPERCONDUCTIVITY OF ULTRATHIN ALLOY FILMS FROM BULK IMMISCIBLE ELEMENTS	46
4.1. Introduction	47
4.2. Experimental Procedures	48
4.3. Results and Discussions	48
4.4. Summary	56
5. INFLUENCE OF INTERFACE RECONSTRUCTION ON SUPERCONDUCTIVE PROPERTIES IN ULTRATHIN FILMS	57
5.1. Introduction	58
5.2. Experimental Procedures	59
5.3. Results and Discussions	60
5.4. Summary	66
6. QUANTUM SIZE EFFECTS ON THE EXCITATION AND DAMPING OF VOLUME PLASMONS IN ULTRATHIN FILMS	67
6.1. Introduction	68
6.2. Experimental Procedures	69
6.3. Results and Discussions	70
6.4. Summary	77

List of References

Vita

List of Figures

1.1. STM images of (a) the Ge/Si(100)- $2 \times n$ surface showing dark vacancy lines perpendicular to the Si dimer rows. The image size is $100 \times 100 \text{ nm}^2$ (Image from [Wang, 2002a]), (b) the Si(553)-Au surface showing atom-wire segments. The image size is $37.5 \times 37.5 \text{ nm}^2$ (Image from [Crain, 2006], and (c) the Si(112)- $n \times 1$ -Ga surface (Image from [González, 2004]).	3
1.2. Schematic view of the three thermodynamically distinct epitaxial growth modes. (a) Volmer-Weber (VW) growth. (b) Frank-Van der Merwe (FV) growth. (c) Stranski-Krastanov (SK) growth.	5
1.3. Illustration of discrete electronic quantum well states. (a) The film thickness reduces nanometer scale. Electrons are confined between the two boundaries of the film (surface and interface). (b) Probability densities for the $n = 1, 2$, and 3 quantum well states of a particle confined in a one-dimensional box of size d .	6
1.4. Calculated relative surface energy per surface atom as a function of layer thickness N . (a) freestanding Pb films. (b) Pb films on Si. The dotted curves represent envelope functions for the quantum oscillations (Image from [Hong, 2003]).	7
1.5. Schematic of a novel two-dimensional growth mode and nanostructure formation on vicinal surfaces. (a) Two-dimensional FV growth mode or row-by-row growth. (b) Two-dimensional SK mode, or row-by-row followed by island growth. (c) Two-dimensional VM mode, or island growth (Image from [Li, 2000]). (d) CaF_2 stripes on top of stepped silicon, which has been coated by a CaF_1 layer. (e) Linear array of CaF_2 dots on stepped silicon (Image from [Himpsel, 2001]).	9
1.6. Flowchart of this thesis.	11
2.1. Schematic illustration of the PES experiment. Ejected electrons from core levels are dispersed by an electron energy analyzer and counted by a channeltron detector. The spectrum represents the kinetic energy distribution of the emitted photoelectrons (i.e. the number of emitted photoelectrons as a function of their kinetic energy).	15
2.2. When a sample surface is irradiated with monochromatic x-rays, the core levels are ionized and photoelectrons are emitted from the surface.	16
2.3. Calibration of the deposition rate of Pb on Si(111). The kink corresponds to the completion of the β -phase. The substrate temperature is $250 \text{ }^\circ\text{C}$.	17
2.4. Electron inelastic mean free path (IMFP), λ , of as a function of the electron's kinetic energy. The "universal curve" of IMFP in solid state materials is indicated by the broken line. The	

IMFP has a minimum near 50 - 100 eV. The IMFP values can be obtained from the universal relation which is $\lambda_m = 538E^2 + 0.41(aE)^{1/2}$ for elements [Seah, 1979].	19
2.5. Schematic illustration of LEED. (a) An electron gun produces low energy electrons impinging onto the sample surface. The beam scattered from the sample surface passes a set of biased grids, filtering out the inelastically scattered electrons, and is subsequently accelerated towards a fluorescent screen. When electrons strike the screen, they cause the phosphor to glow revealing the diffraction pattern. (b) Scattering from a periodic lattice (see text).	20
2.6. (a) Ewald sphere construction in 2D. (b) Ewald Sphere Construction for LEED	22
2.7. Schematic view of a STM. The heart of the STM consists of a very sharp tip whose position is controlled by piezoelectric elements. By applying a voltage between the tip and sample, a tunneling current flows when the tip-sample distance is reduced to a few atomic distances. (inset : Observation of metallic nano particles in the constant current mode.)	24
2.8. Energy level diagram of the tunnel junction between a metal tip and metal surface. The left hand side of the figure represents a negatively biased sample, whereas the right hand side represents a positively biased sample. Electrons occupying states within the energy window ΔE can tunnel from the sample to the tip and from the tip to the sample, respectively. Φ_S and Φ_T are the barrier heights for the sample and tip, and z is the width of the tunnel gap.	24
2.9. Sketch of a tip with two protrusions.	25
2.10. (a-b) dc SQUID. (c) The rf SQUID inductively coupled to its tank circuit.	26
2.11. (a) A second-order gradiometer. (b) The magnetic flux induced by a dipole moving along the axis z of the coils generates a typical voltage reading from the pick-up coils.	27
2.12. (a) LEED pattern (70 eV) and (b) STM image of the Si(111)- 7×7 surface. (c) The dimer-adatom-staking fault (DAS) model by Takayanagi et al [Takayanagi, 1985]. Side view: atoms in the lattice plane along the long diagonal of the surface until cell are shown with larger circles than those behind them. Top view: atoms in (111) layers at increasing depth are indicated by circles of decreasing sizes. The green circles represent the 12 adatoms per unit cell, and the 6 rest atoms are shown as dark green circles. The right half of the unit cell contains the stacking fault.	29
2.13. (a) LEED pattern (55 eV) (Image from [Čechal, 2007]) and (b) STM image ($7 \times 7 \text{ nm}^2$) (+2V) (Image from [Hibino, 1996]) of the Si(111)- $\sqrt{3} \times \sqrt{3}$ -R30°-Ga surface. The Ga coverage is 1/3 ML	31
2.14. (a) T_1 model, (b) H_3 model, (c) T_4 model, and (d) side view of the T_4 model for the 1/3-ML phase. Chemisorbed adatoms are shown in black. Si atoms in the first and second layer below the adatoms are shown in white and gray, respectively. Only the first two layers of the Si substrate are shown in the top view illustrations. For the side view illustration, the top four layers of the Si substrate are shown. The 1×1 unit cell is indicated by dotted lines and the ($\sqrt{3} \times \sqrt{3}$) unit cell is indicated by dashed lines. The top view and the side view are not drawn at the same scale (Image from [Chan, 2003]). (e) STM images containing mixed domains of Si(111)- $\sqrt{3} \times \sqrt{3}$ -R30°-Pb and Si(111)- 7×7 , recorded at a sample bias of - 0.5 V. A	

schematic illustration of the area inside the red hexagon is shown on the right side.	32
2.15. (a) Phase diagram of a monatomic Pb layer on Si(111) in the coverage range $1.2 \text{ ML} < \theta < 1.33 \text{ ML}$ (Image from [Stepanovsky, 2006]). (b) Corresponding LEED patterns. Stepwise deposition experiments at constant temperature ($\sim 169 \text{ K}$) reveal the formation of the various (n, m) commensurate phases following the Devil's Staircase hierarchy. (c) Schematic model of the $(\sqrt{3} \times \sqrt{3})$ and $(\sqrt{7} \times \sqrt{3})$ structures. Pb atoms at high symmetry positions (H_3) are shown in red.	33
3.1. STM images of the Ga-covered Si(112) $n \times 1$ surface: (a) $n = 5.49$, (b) $n = 5.68$, and (c) $n = 5.88$	37
3.2. (a) Top view and (b) side view of a ball and stick representation of the Si(112)- 6×1 -Ga surface. (Figure from [González, 2004]).	39
3.3. Normalized distributions of $m \times 1$ unit cells on the surface, fitted with Gaussians. The centroid of Gaussian distribution shifts from $n = 5.28$ to $n = 5.95$ with increasing μ . Their standard deviations are $\sigma = 0.49 \pm 0.02$. Inset: $u_{m \times 1}$ [in eV; see Eq. (3.1)] versus $1/m^2$ for $m = 4, 5, 6, 7$, and 8 from DFT calculations for $\mu = -0.55 \text{ eV}$	40
3.4. LEED intensity profiles of the Ga-covered Si(112)- $n \times 1$ surface (70 eV). The average $n \times 1$ periodicities determined from the intensity profiles are indicated on the right. Dotted lines follow the continuous shifts of the fractional order spots. Inset: sections of the LEED image for $n = 5.97$ and $n = 5.21$	40
3.5. Schematic drawing of different kink configurations. Light/dark rectangles represent $6 \times 1/5 \times 1$ unit cells. (a) <i>Regular</i> kink, (b) <i>nonregular</i> kinks (see text). (c) and (d) Two possible configurations for the model system used in our analysis. Circles in (a)–(d) highlight kink positions. (e) Shows a portion of the oblique lattice used in the DFT calculations of the kink energy (oblique lattice vectors indicated by arrows).	44
4.1. STM images of (a) a $6.9 \pm 0.2 \text{ ML}$ deposit showing only 6 ML deep holes ($500 \times 500 \text{ nm}$), and (b) a $8.5 \pm 0.2 \text{ ML}$ deposit showing only 8 ML deep holes ($500 \times 500 \text{ nm}$). Layer thicknesses are indicated in each panel and are measured from the Si(111) surface. (c) Thickness dependent surface energy of $\text{Pb}_{1-x}\text{Ga}_x$ for $x = 0.06$ films (filled squares) and of pure Pb films (open squares) from DFT.	49
4.2. (a) Ratio of the Ga and Pb core level intensity as a function of temperature for a $8.5 \pm 0.2 \text{ ML}$ deposit. The dashed horizontal line corresponds to the measured intensity ratio when Ga ($\sim 0.5 \text{ ML}$) is deposited prior to Pb ($\sim 8.0 \text{ ML}$). Error bars reflect the spread of values over five experimental runs. (b–d) STM images ($700 \times 700 \text{ nm}$) obtained at three particular temperatures indicated in (a).	50
4.3. (a) Critical temperature as a function of inverse film thickness: $\text{Pb}_{1-x}\text{Bi}_x$ ($x = 0.11$ (filled squares) and 0.2 (open squares)), pure Pb (circles), and $\text{Pb}_{1-x}\text{Ga}_x$ ($x = 0.06$) (triangles) obtained from the onset of the real part of the ac magnetization (data of pure Pb and PbBi alloy films were taken from ref. [Ozer, 2007]). (b) Extrapolated bulk T_c versus the average number of electrons per atom. (c) Critical thickness for the onset of superconductivity, d_c , versus the bulk T_c . (d) The offset $T_{c0} - T_c(d)$ as a function of the inverse mean free path ($1/l$).	52

4.4. (a) Magnetization loops at different temperature for a 10 ML alloy film with 8 ML-deep voids. (b) Imaginary part of the ac magnetic response measured with the ac field amplitudes shown. (c) Critical current densities obtained from the DC magnetization loops at 5 Oe in (a) and by fitting χ'' versus $2h_{ac}/J_c d$ to the critical state model, according to Clem and Sanchez [Clem, 1994]).	54
4.5. (a) Normalized χ'' vs ac amplitude at different temperatures of a 10 ML Pb-Ga alloy film and an ideal Bean-type superconductor in disk-shape. (b) Fitting χ'' versus $2h_{ac}/J_c d$ to the critical state model, according to Clem and Sanchez [Clem, 1994].	55
5.1. STM images of a 7.5-ML-deposited $\text{Pb}_{1-x}\text{Ga}_x$ alloy film on the $\sqrt{3}$ -Pb interface (a) and $\sqrt{3}$ -Ga interface (b), showing atomically smooth mesas bounded by 1 ML-high steps. The image sizes are $(300 \times 300) \text{ nm}^2$ and $(500 \times 500) \text{ nm}^2$, respectively. (c) STM image of a 7.5 ML $\text{Pb}_{1-x}\text{Ga}_x$ alloy film on Si(111)- 7×7 showing an atomically smooth film with large 8-ML deep holes. The image size is $(700 \times 700) \text{ nm}^2$. (d) STM image of an 8 ML deposited pure Pb film showing 2 ML-tall mesas. The image size is $(700 \times 700) \text{ nm}^2$ (from [Özer, 2006b]).	60
5.2. dc Magnetization loops at 2 K of 7.5 ML thick $\text{Pb}_{1-x}\text{Ga}_x$ ($x \leq 0.06$) alloy films, grown on Si(111) 7×7 (■), $\sqrt{3}$ -Pb (▼) and $\sqrt{3}$ -Ga (▲). Previously published data for pure Pb films on Si(111) 7×7 exhibiting 2-ML tall mesas (○) or 2-ML deep voids (◇) are shown for comparison (from [Özer, 2006b]).	62
5.3. Imaginary part m'' of the ac magnetic response of a 8-ML-thick $\text{Pb}_{1-x}\text{Ga}_x$ alloy film grown on (a) Si(111)-(7×7), and (b) the $\sqrt{3}$ -Ga interface, measured in 5 G dc field. Dotted gray lines trace the locations of the peaks in m'' .	63
5.4. $H_{c2}(T)$ values of pure Pb and $\text{Pb}_{1-x}\text{Ga}_x$ alloy films for the various interface reconstructions. The nominal coverages are 7.5 ML for Pb-Ga alloy films and ~ 8 ML for pure Pb films. $H_{c2}(T)$ was obtained from the onset of diamagnetic screening as a function of temperature, in various dc fields. The data were measured using a 10 mG probing amplitude	65
6.1. Photoelectron intensity as a function of kinetic energy of the Mg 1s core level for film thicknesses in the range 2-25 ML. Surface and bulk plasmon losses as well as higher order loss satellites are seen on the low kinetic energy side of the spectra. Red lines roughly indicate the positions of the no-loss and bulk plasmon peaks. Their kinetic energy difference corresponds to the plasmon loss energy, which is plotted as a function of film thickness in the inset	70
6.2. Bulk plasmon energies plotted as a function of q_z^2 . Each dotted line is labeled by the quantum number n which is used to calculate the corresponding q_z values. Only the solid line reproduces the bulk dispersion relation (see text).	71
6.3. Intensity of the main peak (a) and bulk plasmon satellite (b) as a function of film thickness. The satellite intensity is normalized to the intensity of the main peak. Solid curves show best fits to the data	73
6.4. Kinetic Energy (a), Lifetime broadening (b), and Asymmetry parameter (c) of the no loss peak obtained from fittings to Doniach-Šunjić lineshapes	76

CHAPTER 1

Introduction

“Natural processes should be judged different from mechanical ones because they are self-organizing”.

by Immanuel Kant

1.1. *Self-organizing systems*

Nanostructured systems have a remarkable impact in our everyday lives. Today's latest technology depends on the ability to control materials on very small length scales to enhance their performance and to produce new functional properties and applications. The tools to accomplish this trend are so-called "top-down" and "bottom-up" techniques. In contrast to top-down fabrication, which is a very difficult method for manufacturing at the nanoscale level, bottom-up synthesis establishes new features from fundamental building blocks, usually spontaneously with the self-assembly and self-organization of crystal surface structures, without the need for patterning. A common practice for realizing these events is to use templates on which each nanostructure develops in a controlled fashion.

If the system *self-organizes*, pattern formation and organization (including naturally imposed chemical and physical constraints, redundancy and/or formation of new complex structures) at the global level develops solely by interactions between the lower level components rather than by interactions with the external environment. The realization of the relevance of this phenomenon dates back to René Descartes, a 17th-century French philosopher, mathematician, physicist and writer. Descartes thought that organization was inevitable in a given condition even though the system may not seem to have a tendency for organization. This idea stemmed from his belief that the ordinary laws of nature led the system to organize [Vartanian, 1953]. Based on this idea, the term "self-organization" was used by Immanuel Kant, an 18th-century German philosopher when he argued that the "organs" or "instruments" of an entity produce its other parts reciprocally and, consequently, it governs its own formation. The first use of the notion of "self-organizing systems" in contemporary science was by W.R. Ashby [Ashby, 1947]. The concepts and terminology of self-organization have been widely used in the modern scientific literature though its precise or intended meaning may vary, depending on the scientific discipline. While it may seem that self-organization would be opposed by the tendency of nature to maximize entropy or disorder, thermodynamically open systems such as biological systems constantly exchange entropy with their surroundings and, consequently, can display various levels of self organization. Examples include cellular automata, distributed robotics, nanotube arrays and self-assembled monolayers.

In this thesis, we will elucidate the driving forces of self-organization in a variety of thin film material systems and explore experimental methods that can influence or even tailor the possible outcome of the self-organization process. This "*controlled self-organization*" will be highly

useful in designing bottom-up synthesis pathways of artificial nanostructured materials and devices.

1.2. Self-assembly formations in hetero-epitaxy

Two types of controlled self-assembly mechanisms will be introduced in this section; (a) classical assembly of atom vacancies into quasi one-dimensional line structures and (b) quantum-driven assembly of atoms into atomically-smooth two-dimensional thin films. In principle, classical and quantum mechanical driving forces may play a role in both systems. However, the experimental conditions are chosen in such a way that only one of these mechanisms will be dominant.

1.2.1. *Self-assembly of atom vacancies*

The first example is the formation of atom vacancies in a monatomic surface layer and their subsequent organization into quasi one-dimensional line features. Figure 1.1(a-c) shows three examples. The scanning tunneling microscopy (STM) image in Figure 1.1(a) reveals the formation of (dark) atom vacancies when growing an ultrathin Ge layer on Si(100). These vacancies are created to minimize compressive strain in the surface layer, which arises from the lattice mismatch between Si and Ge. Amazingly, the individual vacancies self-organize into

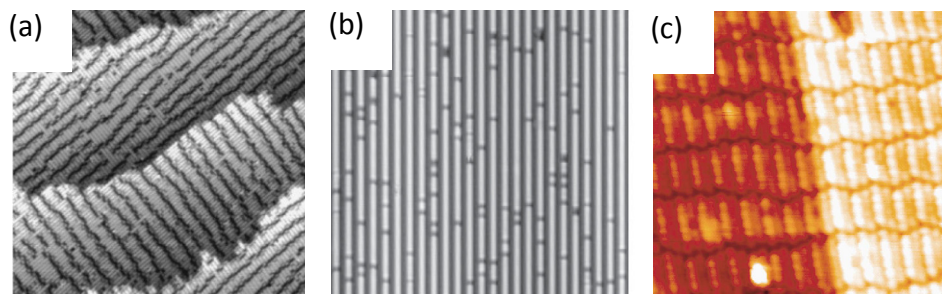


Figure 1.1

STM images of (a) the Ge/Si(100)- $2 \times n$ surface showing dark vacancy lines perpendicular to the Si dimer rows. The image size is $100 \times 100 \text{ nm}^2$ (Image from [Wang, 2002a]), (b) the Si(553)-Au surface showing atom-wire segments. The image size is $37.5 \times 37.5 \text{ nm}^2$ (Image from [Crain, 2006], and (c) the Si(112)- $n \times 1$ -Ga surface (Image from [González, 2004]).

more-or-less regularly spaced quasi one-dimensional vacancy lines, resulting in a long-range ordered $2 \times n$ superstructure. The value of n depends on the Ge coverage and can be varied almost continuously. This phenomenon has been studied extensively [Tersoff, 1992; Kohler, 1992; Butz, 1992; Wang 2002; Nurminen, 2003; Beck, 2004]. The driving mechanism of this remarkable self-organization phenomenon is rooted in the elastic repulsion between vacancies along the [110] direction of the substrate and the effective attraction between vacancies in neighboring dimer rows. The vacancy lines are not perfectly straight because entropy opposes self-organization and disorder will be frozen in well above room temperature. The frozen meandering of the vacancy lines can be analyzed quantitatively using mean field theory, meaning that the meanderings of neighboring vacancy lines are uncorrelated.

Figure 1.1(b) shows a similar phenomenon. This time, the system consists of Au-induced “atom wires” on a Si(553) surface. A remarkable feature is that the vacancies are no longer ordered. However, the size distribution of the Au wire segments appears to be dominated by quantum size effects in the short chain segments [Crain, 2006]. Finally, Figure 1.1(c) shows the meandering vacancy lines in a monatomic Ga layer on Si(112). This system will be analyzed in Chapter 3. At first sight, this system seems similar to Ge on Si(100) and there is no clear evidence that quantum size effects play a role in the self-organization phenomenon. However, as we will show, a major distinction is that the meandering appears to be dominated by vacancy-vacancy correlations. We furthermore show that the mean distance between vacancy lines can be tuned experimentally by changing the deposition conditions.

1.2.2. Self-assembly of atoms in classical film growth

The second example entails epitaxial thin film growth. Epitaxial film growth is an old example of thermodynamically-driven self-assembly. Ideally, one would like to control film growth with monolayer precision, meaning that the film material should grow layer-by-layer. However, this hardly ever happens. Particularly, metals on semiconductors have more complex growth morphologies.

From a thermodynamic point of view, one can distinguish three distinct growth modes: Frank-Van der Merwe (FV) growth, Stranski-Krastanov (SK) growth and Volmer-Weber (VW) growth, as shown in Figure 1.2. FV growth follows the layer-by-layer sequence. SK growth refers to initial layer-by-layer growth, followed by three-dimensional islanding. VW growth refers to three-dimensional islanding right from the start [Zangwill, 1988]. These growth modes are

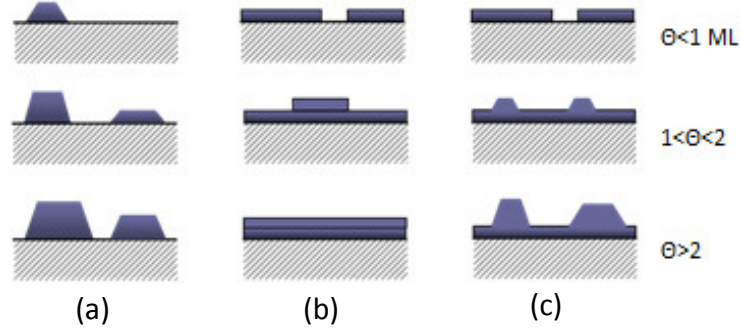


Figure 1.2

Schematic view of the three thermodynamically distinct epitaxial growth modes. (a) Volmer-Weber (VW) growth. (b) Frank-Van der Merwe (FV) growth. (c) Stranski-Krastanov (SK) growth.

determined by the relative magnitudes of the binding energy between the adsorbate atoms and the substrate, E_s , and the binding energy between adsorbate atoms, E_a . In addition, the lattice mismatch between the film and the substrate also affects the growth mode because the built-up strain will ultimately drive a strain-relaxation transition resulting in a three-dimensional morphology. When $E_s > E_a$, the deposited atoms strongly bond to the substrate so that two-dimensional clusters are formed. On the other hand, islands are formed when $E_s < E_a$ so that the deposited atoms are more strongly bound to each other. This is the usual growth mode for metals on semiconductors or insulators, even for lattice-matched systems such as Fe on GaAs [Chambers, 1986; Filipe, 1997]. As we will show in the next Section, the three dimensional morphology of metals on semiconductors can be avoided. It requires designing a kinetic pathway toward stabilizing a two-dimensional morphology by exploiting quantum mechanical confinement. These so-called quantum films are not stable from a thermodynamic view point. However, they are metastable and can thus be realized under special experimental conditions.

1.2.3. *Self-assembly of atoms in quantum growth*

Quantum size effects (QSE) in the formation and stability of metallic nanostructures on semiconductor surfaces have been studied over the past several years. As the size of a metallic nanostructure shrinks to interatomic distances or the electron's wavelength, electrons are confined between the potential barriers in the direction perpendicular to the surfaces of the nanostructures (Figure 1.3(a)). This electronic confinement produces discrete electron states or quantum well

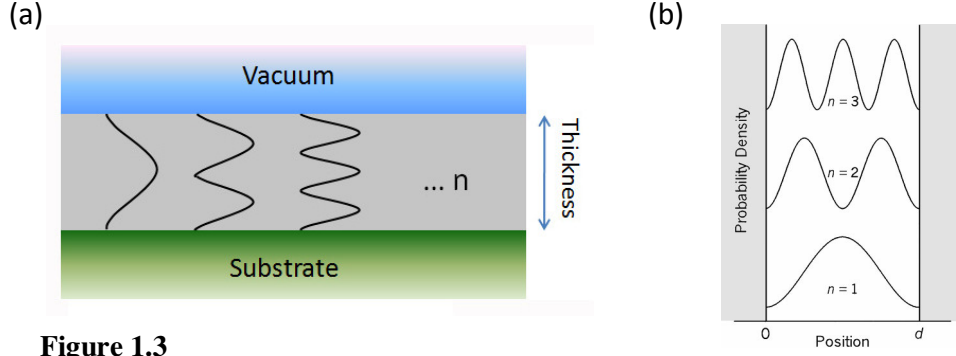


Figure 1.3

Illustration of discrete electronic quantum well states. (a) The film thickness reduces nanometer scale. Electrons are confined between the two boundaries of the film (surface and interface). (b) Probability densities for the $n = 1, 2$, and 3 quantum well states of a particle confined in a one-dimensional box of size d .

states. Here we study an ultrathin metal film in which the vertical motion is confined as in a one-dimensional square-well potential. The correspondent probability density in the films is shown in Figure 1.3(b). The wave vectors are $k_n = \frac{n\pi}{d}$, where n is an integer quantum number ($n = 1, 2, 3, \dots, n_0$) and d is the film thickness. The energy levels are given by $E = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2}{2m} \left(\frac{n\pi}{d} \right)^2$, where m is the free electron mass. The wave functions are $\psi(z) \propto \sin\left(\frac{n\pi z}{d}\right)$.

The quantum size effect can have profound influences on the low-temperature epitaxial growth of a metal film. In spite of the thermodynamic bias toward the SK growth mechanism, quantum size effects help stabilize atomically smooth metal films on e.g., Si(111), Ge(111), Cu(111) and GaAs(110) at low temperature [Hinch, 1989; Grottini, 1997; Hong, 2003; Smith, 1996]. Pb on Si(111) is the most studied case [Yeh, 2000; Hong 2003; Özer, 2005].

The importance of quantum size effects in thin film growth was already indicated in early jellium-model calculations of a thin metal slab by Schulte in 1976. The calculations indicated the existence of quantum oscillations in the electron density, potentials, and work function with a period of $\frac{\lambda_F}{2}$ where λ_F is the Fermi wavelength [Lang, 1971; Schulte, 1976; Feibelman, 1983]. However, because the film thickness of real materials is atomically-discrete, it is expected that quantum oscillations cannot be seen in materials for which $d = \frac{n\lambda_F}{2}$ [Feibelman, 1983] whereas the oscillations should be profound in materials with $d = (2n - 1) \frac{\lambda_F}{4}$.

Pb grown on Si(111) exhibit a quasi bilayer-by-bilayer growth mode at low temperature, as opposed to the classical SK growth seen at room temperature and above [Özer, 2005]. The bilayer periodicity originates from the fact that the Fermi wavelength and atomic layer spacing are nearly commensurate, according to $2d \approx 3\lambda_F/2$ where the interlayer spacing d is 2.86 Å and the Fermi wavelength λ_F is 3.95 Å. Pb films on Si(111)-7×7 are stable between 6 and 14 ML only if the number of atom layers is even. Between 15 and 24 ML films are stable if the number of atoms layers is odd. This even-odd switching in the film stability can be attributed to the beating of the atomic layer spacing and Fermi wavelength.

First-principles calculations of Pb on Si(111) confirm this picture [Hong, 2003]. Figure 1.4 shows the calculated surface energy $E_s(N)$ which is obtained by subtracting from the total energy of the model slab an energy term that is linear in the film thickness. The envelope curves (dotted lines) highlight the long-wave beating pattern and the even-odd crossovers in the thin film stability. The actual location of the even odd crossover or “phase shift” is strongly affected by the boundary condition, as shown in Figure 1.4(a) and (b) for free-standing films and for films on a Si(111) substrate, respectively. This special quantum morphology has a major impact on the system’s physical properties and has, for instance, lead to the realization of a robust superconductive state and demonstrations of quantum oscillations in the surface chemical reactivity [Ma, 2007].

As mentioned previously, the quantum growth morphology is metastable meaning that the morphology corresponds to a local minimum in the Gibbs free-energy landscape. These

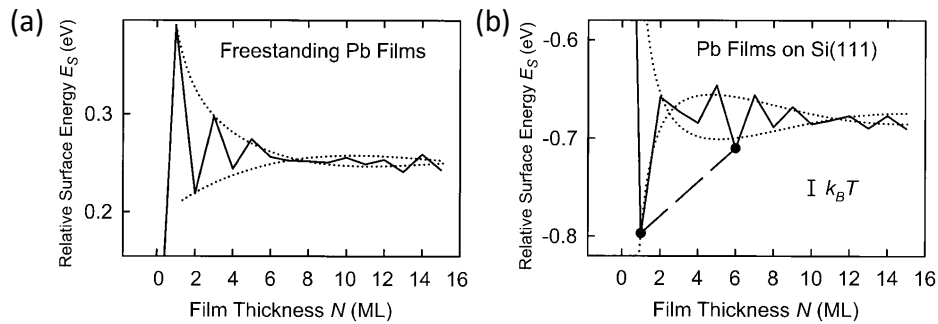


Figure 1.4

Calculated relative surface energy per surface atom as a function of layer thickness N . (a) freestanding Pb films. (b) Pb films on Si. The dotted curves represent envelope functions for the quantum oscillations (Image from [Hong, 2003]).

atomically smooth films are usually created in a two-step process: deposition onto a cold surface, followed by a mild thermal annealing to temperatures that are typically of the order of 200-250 K. This procedure gives the adatoms enough mobility to smoothen the film so that it acquires its metastable quantum morphology. When the annealing temperature is too high, the film will acquire the thermodynamically favored SK morphology. So while the adsorbate atoms self-organize into atomically smooth films, due to the quantum size effect, the experimentalist does exert some external control in choosing the annealing temperature and boundary conditions. The latter can be done by choosing the substrate and/or capping layer and by modifying the reconstruction of the buried interface.

1.3. Experimental control

For application purposes, it will be highly desirable to acquire some experimental control on the self-organization process so that one could ultimately tune the physical properties of these thin film nanostructures. Besides the usual control of growth parameters such as temperature, pressure, and flux, we employ two other methods to alter the structure and properties of these materials, namely template modification and chemical doping.

1.3.1 *Template modification*

The interface structure determines the interface energy of thin-film hetero-structures and thus affects their overall morphology. Therefore, by controlling the interface structure prior to hetero-epitaxial growth, it is possible to tune the properties of a thin-film nanostructure. Figure 1.5 illustrates the possible use of stepped templates for growing a variety of surface based nanostructures.

For instance, one can imagine creating the lower-dimensional analogs of the classical FV, SK, and VW growth mechanisms by using a vicinal substrate [Ball, 1958]. As a specific example, we show the formation of CaF_2 stripes and CaF_2 nanodots at the step edges of a vicinal $\text{Si}(111)\text{-}7 \times 7$ surface in Figure 1.5(d) and (e) [Himpsel, 2005]. The formation of stripes only seems possible, however, through an additional engineering step in which the vicinal $\text{Si}(111)\text{-}7 \times 7$ surface is first coated with a layer of CaF_1 . Elongated islands were grown also on anisotropic surface reconstructions such as Si on $\text{Si}(100)\text{-}2 \times 1$ [Mo, 1998].

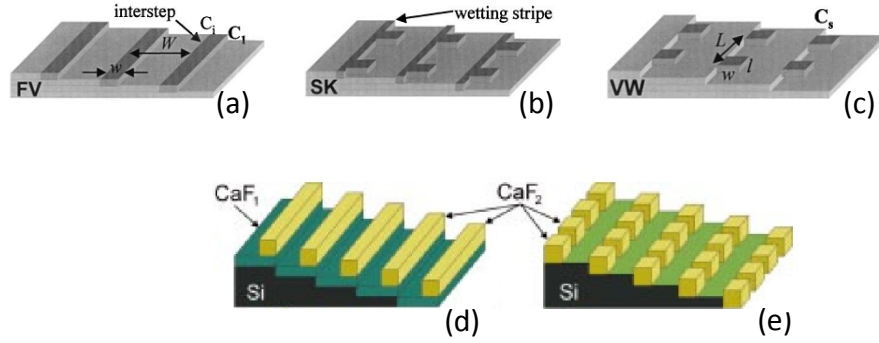


Figure 1.5

Schematic of a novel two-dimensional growth mode and nanostructure formation on vicinal surfaces. (a) Two-dimensional FV growth mode or row-by-row growth. (b) Two-dimensional SK mode, or row-by-row followed by island growth. (c) Two-dimensional VM mode, or island growth (Image from [Li, 2000]). (d) CaF_2 stripes on top of stepped silicon, which has been coated by a CaF_1 layer. (e) Linear array of CaF_2 dots on stepped silicon (Image from [Himpsel, 2001]).

1.3.2 *Chemical doping*

Finally, substitutional doping is proven paradigm for tailoring the properties of functional materials [Özer, 2007]. Textbook examples include the n- and p-type doping of semiconductors, the hole-doping of high temperature superconductors and the fabrication of novel photovoltaic materials for solar energy applications. Doping of nanostructures is much less controlled and understood. The nanoscale dimension likely affects the thermodynamic and kinetic criteria for dopant incorporation, solid solubility limit, carrier scattering and quantum effects. Recently, our group succeeded in doping Pb-based quantum films via Bi substitution. Because Bi is right next to Pb in the periodic table, Bi incorporation translates into n-type doping and it was shown that the doping affects the Fermi wave vector and hence the electronic stability criterion and growth mode of the film. In this thesis, we will explore the issue of solid solubility and doping in the quantum regime.

1.4. Scope and overview of the thesis

Nanostructures are particularly interesting as building blocks for artificial superstructures with precisely engineered physical properties. Engineering or device applications of these

ensembles of nano objects require a great level of control of the size distribution and uniformity of the individual nano objects. This in turn implies that one first needs to establish the mechanisms that are driving the self assembly. Secondly, one needs to establish the structure-property relationships, and in the third place, one would like to explore how the structure and properties might be tunable. All three aspects will be addressed in this thesis. We are particularly interested in how the *collective* physical properties emerge as these nanosystems grow in size. To this end, we will focus on the superconductive properties and plasmonic excitations in these films. Apart from our academic interest into the emergence of these collective properties, they are also of practical interest, for instance in the development of superconducting qubit devices or nanoscale optoelectronic devices.

In the previous sections, we highlighted two intriguing forms of self organization in thin film hetero-epitaxy. The first entailed the self organization of atomic vacancies into a quasi one-dimensional vacancy-line superstructure. The vacancy creation is driven by a strain relaxation mechanism, breaking up the atom wires into atom wire segments. The size distribution of those segments could be attributed to elastic repulsion between vacancies along [110] or to quantum size effects in the individual segments, resulting in preferred segments lengths. The second mechanism entailed the existence of preferred or magic film thicknesses due to the quantum size effect. The systems under consideration are so-called soft metals and lattice strain is expected to play a minimum role. In this thesis, we will analyze the formation and structure of these surface-based nanostructures as a function of the experimental control parameters such as temperature, and flux. We will explore the structure-property relationships with an emphasis on collective phenomena such as superconductivity and plasmon excitations. We employ substitutional doping and interface reconstruction to further tailor the properties of these materials.

Figure 1.6 shows a flowchart of the thesis. The thesis chapters can be read individually if the reader has a particular interest in the topic being presented. Following this introductory chapter, Chapter 2 presents an overview of the experimental tools and methods that are employed in this thesis. In Chapter 3, we will focus on the self-organization of atom vacancies in a monatomic gallium layer on Si(112). This is a wonderful example of near perfect thermodynamic equilibrium growth. The average spacing between the vacancies lines is tunable by adjusting the chemical potential of the gallium atoms through the effusion cell temperature. We observed line spacings that are in excellent agreement with first-principles calculations of the total energy under these experimental conditions (i.e., chemical potential). Entropic fluctuations from the average periodicity are also quantitatively accounted for. The system is unique in the sense that vacancy-

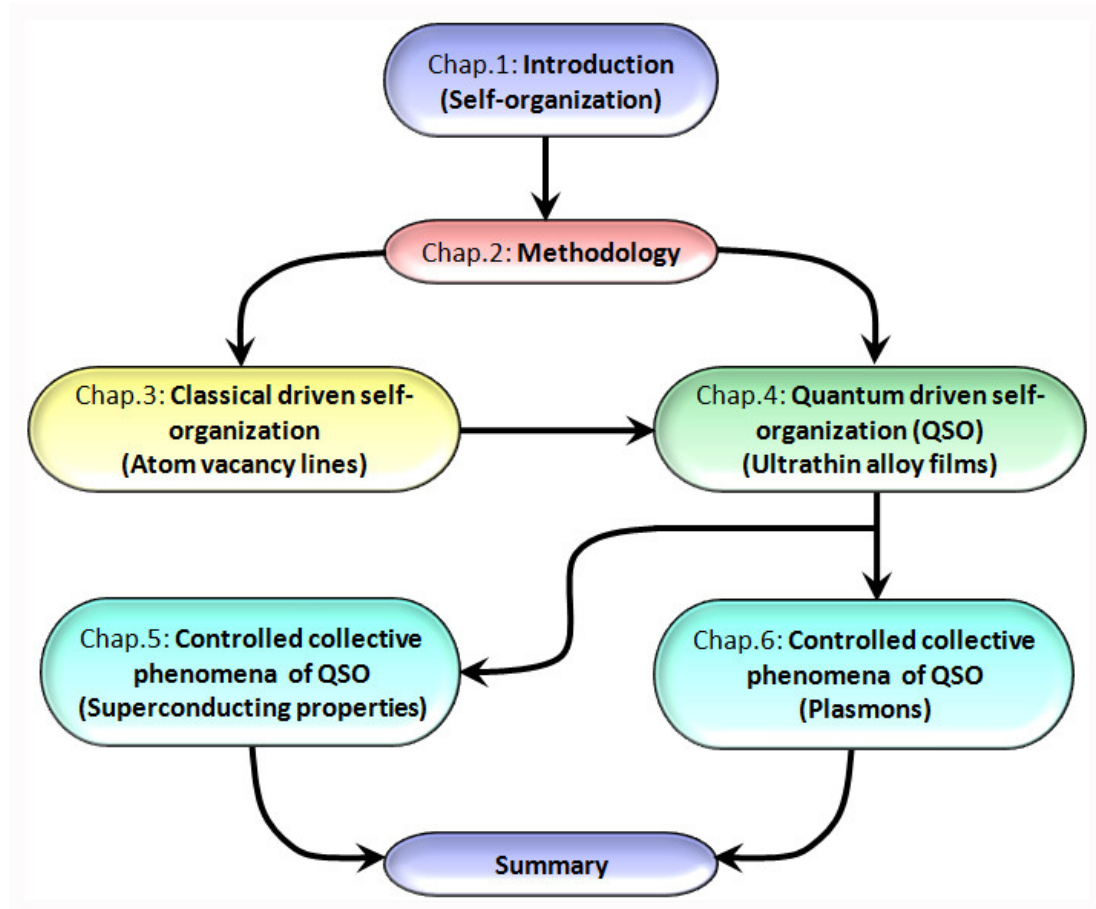


Figure 1.6
Flowchart of this thesis.

vacancy correlations play a very significant role in the self-organization process. We present a new lattice model that quantitatively connects the DFT calculations for perfect periodic structures with the fluctuating disorder seen in experiment.

In Chapter 4, we are exploring self-organization via quantum growth. In previous studies by our group, it has been shown that quantum size effects in Pb can stabilize film morphologies that are atomically smooth over macroscopic distances [Özer, 2005]. We furthermore showed that the quantum growth mode of Pb can be tuned by Bi-doping or electron doping. The stable layer thicknesses for the Pb-Bi alloys were in perfect agreement with the expected changes in the Fermi wave vector. Hence, doping in these system amounts to “Fermi surface engineering”. The

superconducting transition temperatures indicated that Bi effectively enhances the electron-phonon coupling in the films, similar to the electron-phonon coupling in bulk alloys. In those studies, substitutional dopant incorporation seemed natural because Bi is soluble in bulk Pb. In this thesis, we attempt hole-doping with a group III element: Ga. Interestingly, Ga is not soluble in bulk Pb and therefore it was not a-priori clear whether these quantum films can be doped with Ga. We will show, however, that Ga can be incorporated up to at least 6 at.%. Gallium incorporation furthermore changes the quantum growth morphology, leading to the presence of deep holes with diameters of the order of tens of nanometers. This novel growth morphology leads to extraordinarily high critical current densities in the PbGa alloy films. Furthermore, by comparing the superconducting transition temperatures of the PbGa alloy films with those of pure Pb and PbBi alloy films, we acquired important new insights into the mechanism of the T_C suppression in ultrathin films.

In Chapter 5, we explore how template engineering affects the quantum growth and properties of the superconducting critical state in PbGa alloys. We find that removal of the Si(111)- 7×7 interface reconstruction promotes Ga segregation, restores classical layer-by-layer growth, and suppresses the critical current density in the films. Thus it appears that the (7×7) interface reconstruction is a key facilitator for establishing novel doped nanophase materials with enhanced superconductive properties.

In Chapter 6, we explore ultrathin Mg films. Even though quantum size effects are clearly visible in the electronic structure of the films, the films grow according to the classical layer-by-layer growth mode. Mg is not superconducting and we instead focused on another collective property, namely plasmon excitations. We demonstrate the existence of quantized plasmon modes in these films and furthermore showed that the Landau damping of plasmons becomes increasingly important in the ultrathin film limit. The latter is a direct manifestation of the quantum mechanical nature of nano-plasmons and has important consequences for electron and light transmission through ultrathin films.

Much of this research was motivated by the realization that quantum mechanical effects are most profound in low-dimensional systems and should be exploited to push the boundaries of condensed matter physics and materials research. In fact, the discovery and theoretical formulation of the quantum growth concept [Zhang, 1998] more than ten years ago already resulted in a wonderful cross-fertilization of surface science, mesoscopic physics, superconductivity research and even heterogeneous catalysis [Ma, 2007], fields that historically

have been almost mutually exclusive. Our investigations specifically contributed new insights into the role of dopants and interface reconstruction on the formation and functional properties of self-organized quantum films. The demonstrated ability to control these quantum effects could ultimately lead to emergent physical properties that are of great academic interest and technological significance.

CHAPTER 2

Surface Science Methods and Background

In this chapter, I will describe the experimental methods employed in this thesis. The self-organization of atom vacancies on the Ga/Si(112) interface described in Chapter 3 has been studied primarily with Scanning Tunneling Microscopy (STM) and Low Energy Electron Diffraction (LEED). LEED was used to establish the ‘average’ surface structure whereas STM was used to examine short-range and intermediate-range order. The complementary information acquired from both techniques provided the key to analyze the ordering of atomic vacancies, which is driven by classical strain effects. In Chapters 4 and 5, we studied self-organization processes driven by quantum effects. Specifically, we studied the distribution of Ga dopants in ultrathin Pb films using the combination of x-ray photoelectron spectroscopy (XPS) and STM. The superconducting properties of these doped Pb films were studied using a Superconducting Quantum Interference Device (SQUID) magnetometer. This chapter is concluded with a description of the substrates used in our thin film growth studies.

2.1. X-ray Photoelectron Spectroscopy (XPS)

2.1.1. Theoretical Background

Photoelectron spectroscopy is a spectroscopic technique for determining the chemical composition of solid surfaces. In XPS, one examines the core levels of the constituent atoms using soft-x-rays (100 - 1500 eV). In ultraviolet photoelectron spectroscopy (UPS), one examines the shallow valence levels or “band structure” using ultraviolet photons (10 - 100 eV). XPS provides valuable information about the chemical valence, nature of the chemical bond, and the screening dynamics. The most common photon sources for XPS are Mg- $K\alpha_{1,2}$ (1253.6 eV) and Al- $K\alpha_{1,2}$ (1486.6 eV) radiation, generated via 10 keV electron bombardment of a water-cooled Mg or Al anode, respectively.

As shown in Figure 2.1, the main components of the photoemission set-up are the x-ray source, x-ray monochromator, electron-energy analyzer, and multichannel detector. Surface

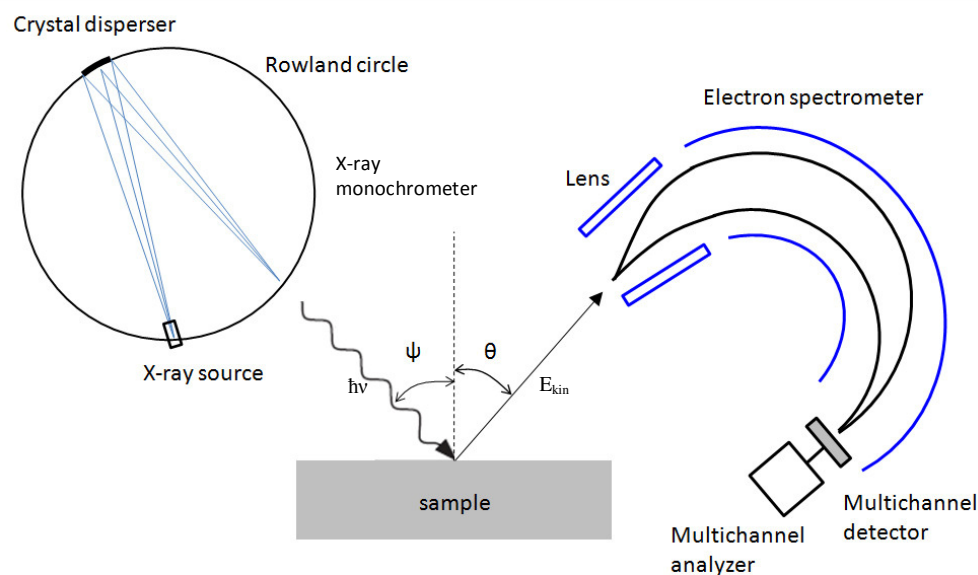


Figure 2.1

Schematic illustration of the PES experiment. Ejected electrons from core levels are dispersed by an electron energy analyzer and counted by a channeltron detector. The spectrum represents the kinetic energy distribution of the emitted photoelectrons (i.e. the number of emitted photoelectrons as a function of their kinetic energy).

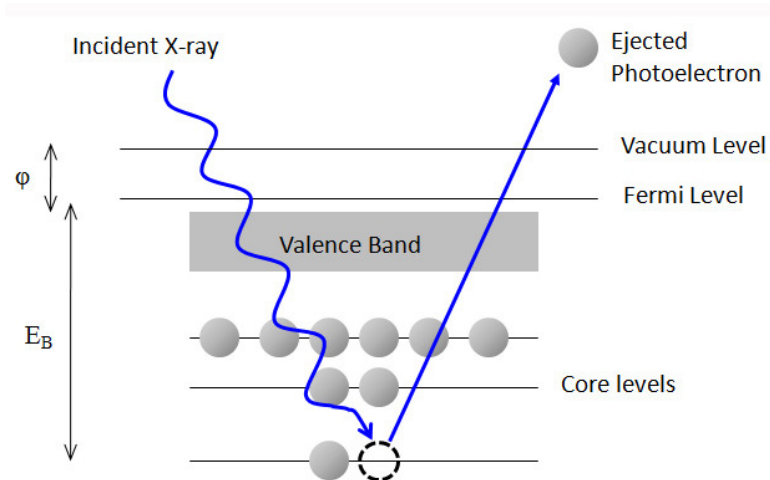


Figure 2.2

When a sample surface is irradiated with monochromatic x-rays, the core levels are ionized and photoelectrons are emitted from the surface.

analysis by XPS involves irradiation of a sample with a focused beam of mono-energetic x-rays. The monochromator (“crystal disperser”) is a bent quartz crystal that not only removes the “Brehmsstrahlung” (or “white” background radiation) and the $\text{Al-K}\alpha_{3,4}$ satellite peaks (originating from doubly ionized atoms in the anode material) via Bragg diffraction but also refocuses the x-rays onto the sample which should be positioned on the Rowland circle (Figure 2.1). The incident radiation generates electrons that are expelled from the core or valence levels of a solid. The emitted electrons subsequently enter an electron spectrometer where their kinetic energy is dispersed before entering the channeltron multiplier. The kinetic energy is given by

$$E_{kin} = \hbar\omega - \phi - |E_B| \quad (2.1)$$

where ϕ is a characteristic constant of the sample known as the work function.

The surface sensitivity of PES is directly related to the small inelastic mean free path of the photoelectrons, λ . In the PES process, some photoelectrons leave the surface without losing kinetic energy while some electrons lose kinetic energy as a result of inelastic collisions with other electrons, phonons, and plasmons. The intensity of the “zero-loss” line follows an exponential decay function [Brundle, 1978],

$$I(d) = K \int_0^d \exp\left(\frac{-x}{\lambda \cos \theta}\right) dx \quad (2.2)$$

where K is constant, and θ is the emission angle.

2.1.2. XPS applications

XPS is a powerful technique for obtaining quantitative information about the composition of the surface layers. In this thesis, XPS was used mainly to calibrate the deposition rate from the Pb and Ga effusion cells and to determine the surface composition of thin alloy films. In order to determine the deposition rate of Pb with XPS, we monitored the growth of the Pb $4f_{7/2}$ core level intensity as a function of deposition time when depositing for Pb on an atomically clean Si(111)- 7×7 surface at 250°C (Figure 2.3). This produces the so-called α and β phases of Pb on Si(111). Because the atomic geometries of the α and β phases are known (see Section 2.5), one can convert deposition time into absolute coverages (1/3 and 4/3 ML, respectively where 1 ML = 7.83×10^{14} atoms/cm²) [Feng, 2004]. Figure 2.3 shows a typical measurement. The kink near 140 seconds marks the completion of the β phase (4/3 ML). The Ga deposition rate was determined by monitoring the Ga $2p_{3/2}$ core level intensity on Si(111) as a function of deposition time at room temperature [Čechal, 2007]. The XPS results were cross-referenced with our STM and LEED data of the Ga/Si(112) - $n \times 1$ interface [González, 2004; Snijders, 2007]. According

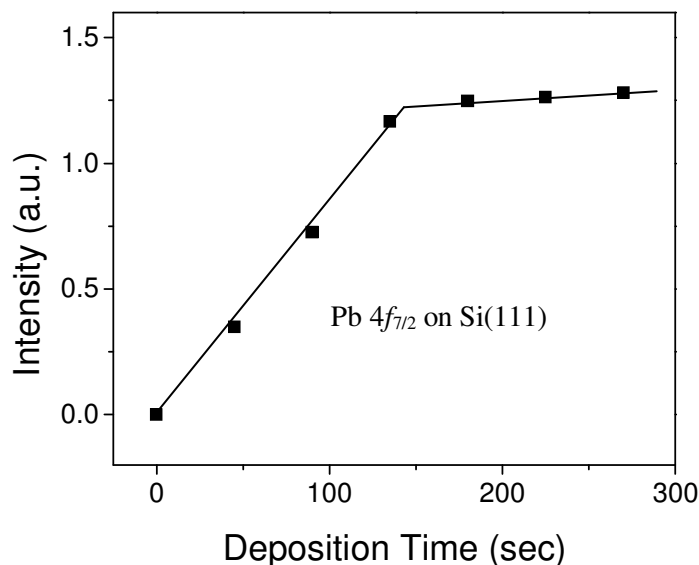


Figure 2.3

Calibration of the deposition rate of Pb on Si(111). The kink corresponds to the completion of the β -phase. The substrate temperature is 250 °C.

to the work presented in Chapter 3, the absolute Ga coverage on Si(112) can be determined from the average period n , which in turn can be obtained from STM and LEED.

We also used XPS to quantify the chemical composition in the outermost (5 nm) layers of the ultrathin $\text{Pb}_{1-x}\text{Ga}_x$ alloy films. While it is difficult in general to deduce the distribution of the Ga atoms directly from the XPS intensities, it is fairly simple to calculate the ratio of the Ga and Pb intensities for an assumed distribution. The calculated values are then compared to experiment. For instance, the XPS core level intensity from a two-dimensional Pb layer should be proportional to the number of Pb atoms (or areal density) in the layer, or $I^{Pb} = \alpha N_{Pb}$ where α is a proportionality constant. If a second atom layer is placed on top, the XPS intensity from the underlayer will be reduced by a factor $\exp(-d / \lambda)$. Accordingly, if n layers are stacked together, the core level intensity becomes:

$$I_n^{Pb} = \alpha N_{Pb} \sum_0^{n-1} \exp(-nd / \lambda) = \alpha N_{Pb} \frac{1 - \exp(-nd / \lambda)}{1 - \exp(-d / \lambda)} \quad (2.3)$$

Next, consider a homogeneous alloy film. The Ga and Pb XPS intensities are given by

$$I_n^{Ga} = \beta N_{Ga} \left(\frac{1 - \exp(-nd / \lambda_{Ga})}{1 - \exp(-d / \lambda_{Ga})} \right) \quad (2.4)$$

$$I_n^{Pb} = \alpha N_{Pb} \left(\frac{1 - \exp(-nd / \lambda_{Pb})}{1 - \exp(-d / \lambda_{Pb})} \right) \quad (2.5)$$

where α and β are proportionality constants and N_{Ga} and N_{Pb} are the average number of Ga and Pb atoms per atom layer, respectively. The proportionality constants α and β take into account the photon flux, photoionization cross section, analyzer transmission, and some other experimental parameters. In principle, α and β could be determined from calibration experiments such as the one shown in Figure 2.4. However, the absolute intensities are very sensitive to the sample position relative to the focal point on the Rowland circle. Therefore, it is more accurate to discuss the *ratio* of the Ga and Pb core level intensities provided they are measured *simultaneously*, i.e., without moving the sample. Taking the ratio eliminates many experimental uncertainties:

$$\frac{I_n^{Ga}}{I_n^{Pb}} = \frac{\beta N_{Ga}}{\alpha N_{Pb}} \times \frac{1 - \exp(-nd / \lambda_{Ga})}{1 - \exp(-nd / \lambda_{Pb})} \times \frac{1 - \exp(-d / \lambda_{Pb})}{1 - \exp(-d / \lambda_{Ga})} \quad (2.6)$$

In Chapter 4, we describe a “cold co-deposition” experiment in which the ratio $N_{Ga} / N_{Pb} = 0.06 / 0.94 = 0.064$ is known from the calibration of our effusion cells (Figure 2.4).

We furthermore know nd from the calibration experiment ($d = 2.86 \text{ \AA}$) and we can calculate λ_{Pb}

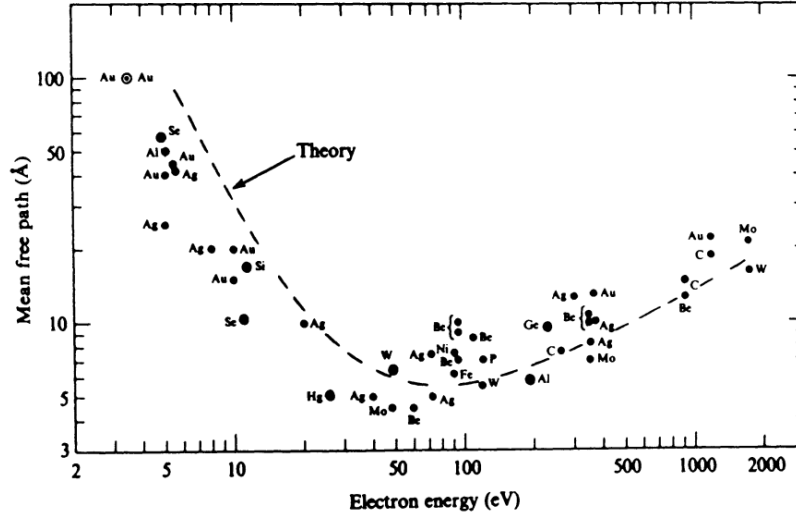


Figure 2.4

Electron inelastic mean free path (IMFP), λ , of as a function of the electron's kinetic energy. The “universal curve” of the IMFP in solid state materials is indicated by the broken line. The IMFP has a minimum near 50 - 100 eV. IMFP values can be obtained from the universal relation $\lambda_m = 538E^2 + 0.41(aE)^{1/2}$ for elements [Seah, 1979].

and λ_{Ga} from the universal IMFP formula. Thus, in the absence of significant atom diffusion at low temperature, we can determine the ratio β/α . Using this ratio, we can now calculate the XPS intensity ratio for any other distribution of Ga.

For instance, let us assume that upon annealing the cold deposit, all Ga atoms in the surface layer exchange position with the Pb atoms underneath so that the surface is fully terminated by Pb. We furthermore assume that the composition in the deeper layers remains unaffected. Then if we count the layers from the substrate, the n th layer or surface layer now has $(N_{Pb} + N_{Ga})$ Pb atoms and zero Ga atoms, and the $(n-1)$ th subsurface layer has $(N_{Pb} - N_{Ga})$ Pb atoms and $2N_{Ga}$ Ga atoms. The intensities of the Pb and Ga core level signal are

$$I_n^{Pb} = \alpha N_{Pb} \left(\frac{1 - \exp(-[n-2]d/\lambda_{Pb})}{1 - \exp(-d/\lambda_{Pb})} \right) + \alpha (N_{Pb} - N_{Ga}) \exp(-d/\lambda_{Pb}) + \alpha (N_{Pb} + N_{Ga}) \quad (2.7)$$

and

$$I_n^{Ga} = \beta N_{Ga} \left(\frac{1 - \exp(-[n-2]d/\lambda_{Ga})}{1 - \exp(-d/\lambda_{Ga})} \right) + 2\beta N_{Ga} \exp(-d/\lambda_{Ga}) \quad (2.8)$$

The ratio of these peak intensities can thus be calculated and compared to experiment. In practice there are many possible distributions of Ga and, consequently, the usefulness of this method for vertical concentration profiling remains limited. However, as we will discover in Chapters 4 and 5, it is possible to distinguish extreme cases of surface segregation, interface segregation and random alloying based on the XPS experiments.

2.2. Low Energy Electron Diffraction (LEED)

2.2.1. *Theoretical Background*

In a LEED experiment, a beam of low energy electrons (typically in the range 20 - 200 eV) impinges onto the sample surface under normal incidence. If the sample surface has a well-ordered surface structure, the backscattered electrons form a diffraction pattern. A typical experimental set-up is shown in Figure 2.5.

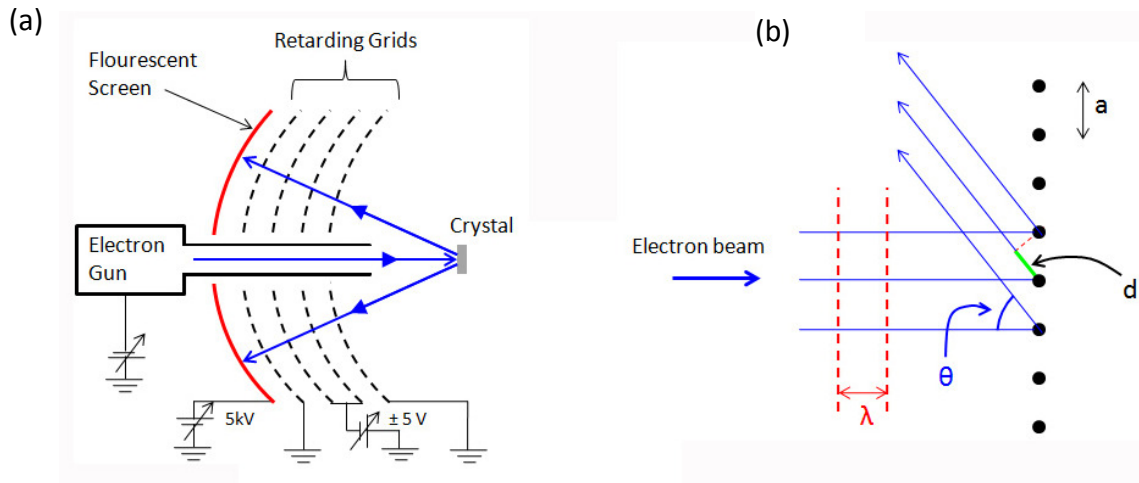


Figure 2.5

Schematic illustration of LEED. (a) An electron gun produces low energy electrons impinging onto the sample surface. The beam scattered from the sample surface passes a set of biased grids, filtering out the inelastically scattered electrons, and is subsequently accelerated towards a fluorescent screen. When electrons strike the screen, they cause the phosphor to glow revealing the diffraction pattern. (b) Scattering from a periodic lattice (see text).

The beam of electrons can be considered as an incident plane wave front, based on the particle-wave duality principle. The electrons are backscattered by the surface atoms, pass through a retarding grid that filters out *inelastically* scattered electrons, and are finally accelerated toward a fluorescent screen. The wavelength of the electrons is given by the de Broglie relation, $\lambda = h / p$ (p is the electron's momentum). The wavelengths of electrons employed in a LEED experiment are comparable to the inter-atomic distances meaning that diffraction effects associated with periodic surface structures can be observed. This can easily be illustrated as follows. Consider the backscattering of a plane wavefront from two adjacent atom rows at the diffraction angle θ (Figure 2.5). The atom rows in Figure 2.5 run normal to the page. As shown in Figure 2.5, the path length difference between backscattered electrons from neighboring atom rows is $d = a \sin \theta$ where a is the distance between the atom rows. Constructive interference of the backscattered electrons requires that $d = a \sin \theta = n\lambda$ where n is an integer and λ the electron's wavelength.

The incident plane wave can be described by

$$\Psi_i = \exp (i\mathbf{k}_i \cdot \mathbf{r}). \quad (2.9)$$

Based on the Bragg conditions for a two-dimensional crystal, the incident electron plane wave of wavelength λ and wave vector $\mathbf{k}_{i\parallel}$ is scattered into a plane wave with wave vector $\mathbf{k}_{f\parallel}$, which is given by

$$\mathbf{k}_{f\parallel} = \mathbf{k}_{i\parallel} + \mathbf{g} \quad (2.10)$$

$$\mathbf{g} = h\mathbf{A} + k\mathbf{B} \quad (2.11)$$

where $\mathbf{k}_{f\parallel}$ and $\mathbf{k}_{i\parallel}$ are the components of the incident wave and scattered wave parallel to the surface respectively, and $\mathbf{g}$ is the 2D reciprocal lattice vector (a scattering vector) which constitutes a linear combination of the primitive vectors of the 2D reciprocal space with integers of h and k . The integers, h and k , are the indices of the scattered plane wave. If the surface structure is long-range ordered, the observed LEED pattern is a direct image of the 2D reciprocal lattice and can be indexed by the integers (h, k). Structural information such as the symmetry and dimension of the surface unit cell are thus easily obtained from the LEED pattern.

The diffraction conditions of Eq. 2.10 and 2.11 can be visualized with the Ewald sphere construction. Figure 2.6 shows the reciprocal lattice of a surface. The reciprocal lattice of a surface consists of a two-dimensional array of diffraction rods as opposed to the three dimensional array of diffraction spots of a bulk crystal because there is no translational periodicity normal to the surface. In the Ewald sphere construction, the wave vector of the

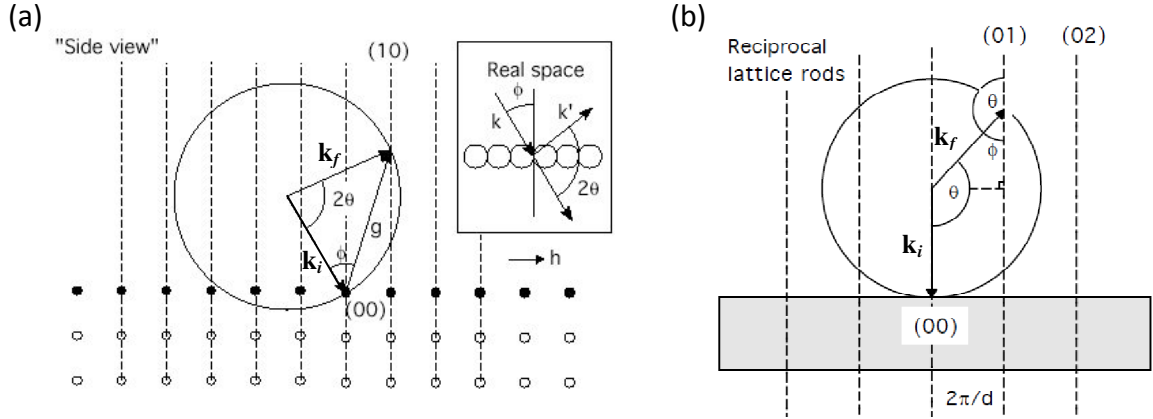


Figure 2.6

(a) Ewald sphere construction in 2D. (b) Ewald Sphere Construction for LEED.

incident beam is pointing at the origin of reciprocal space (see Figure 2.6). The origin of the wave vector $\mathbf{k}_i$ is also the center of a sphere with radius $\mathbf{k}_i = \mathbf{k}_f$. This diffraction sphere is the so-called Ewald sphere. The Bragg conditions of Eq. 2.10 and 2.11 are satisfied when the reciprocal lattice rods and Ewald sphere intersect. In Figure 2.6(b), only integer order spots (rods) are shown. The spacing between the rods is $2n\pi/d$ where d is the in-plane lattice constant. In addition to these integer order spots, we often observe additional spots or fractional order spots that are located in between the integer order spots. For instance, if the translational periodicity on the surface has doubled due to a surface reconstruction, fractional order spots will be located halfway in between the integer order spots.

In LEED, the incident wave can travel into the deeper layers and undergoes multiple scattering events before it emerges as the backscattered wave from the surface. The diffracted plane wave is obtained from the sum of scattered waves which is given by

$$\Psi_f = \sum_g A_g \exp (i\mathbf{k}_g \cdot \mathbf{r}) \quad (2.12)$$

where $\mathbf{k}_g = \mathbf{k}_f$. Analysis of the scattered intensities provides the full structure information.

2.2.2. *LEED applications*

The surface sensitivity of LEED can be attributed to the strong electron-solid interactions for electron energies less than 1 keV. There are two main applications for LEED. The first application is the visual inspection of the surface diffraction pattern. LEED images provide useful information about the structural symmetry and quality of the surface. The second application is quantitative structure determination (atomic coordinates, surface relaxation). This application requires a rather complicated intensity analysis. For this purpose, diffraction intensities are recorded as a function of the incident electron energy and are compared to sophisticated multiple-scattering calculations.

Here, LEED was used to identify the structure of the clean surface, metal-induced surface reconstructions, and the structure of the Pb-based alloy films. Images are recorded with a digital photo-camera or a CCD camera. Diffraction line profiles were analyzed to accurately determine the unit cell dimensions. With a CCD camera, it is also possible to monitor surface phase transitions in real time.

2.3. Scanning Tunneling Microscopy/Spectroscopy (STM/STS)

Scanning tunneling microscope (STM) images not only display the geometrical structure of the surface, but also provide atom-resolved electronic structure information. STM has been the key instrument in providing experimental access to the fascinating nano world. The principle of STM is based on quantum tunneling. When a sharp tip approaches a conducting surface to within say one nanometer, a tunneling current will flow upon application of a bias. The tip is mounted on a piezoelectric tube, which allows for tiny movements by applying a voltage at its electrodes (Figure 2.7). The electronics of the STM system controls the tip position in such a way that the tunneling current and tip-surface distance are kept constant, while simultaneously scanning a small area of the sample surface. This movement is recorded and can be displayed as an image of the surface topography. Under ideal circumstances, the individual atoms of a surface can be resolved and displayed.

As shown in Figure 2.8, all electrons within an energy window ΔE ($= eV_t$, V_t is a bias voltage) contribute to the tunneling current and the electronic structure of the occupied as well as the unoccupied states can be revealed. The principle of STM originates from the tunneling effect in

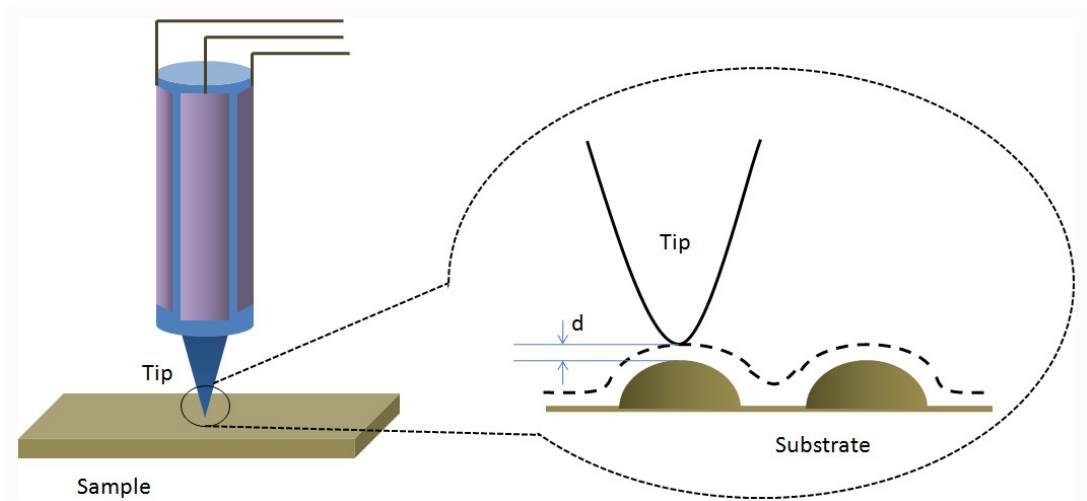


Figure 2.7

Schematic view of a STM. The heart of the STM consists of a very sharp tip whose position is controlled by piezoelectric elements. By applying a voltage between the tip and sample, a tunneling current flows when the tip-sample distance is reduced to a few atomic distances. (inset : Observation of metallic nano particles in the constant current mode.)

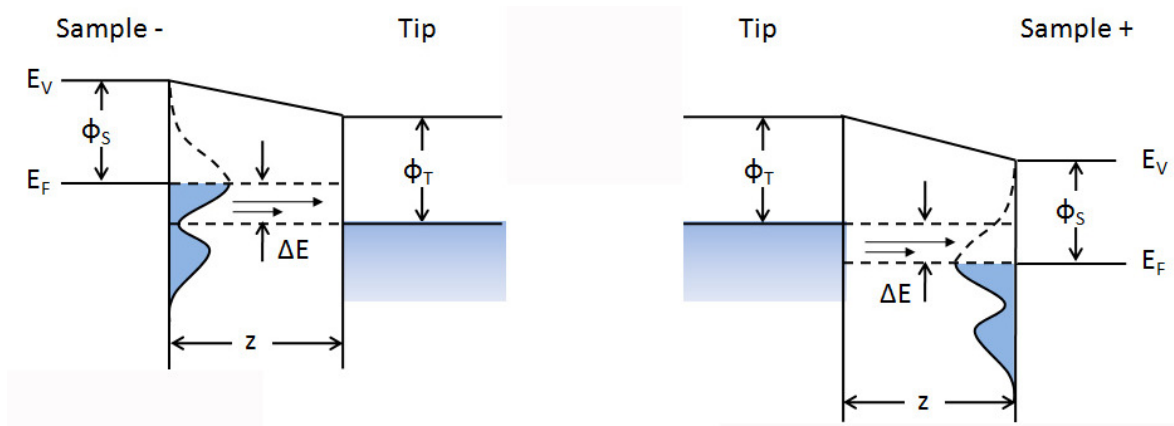


Figure 2.8

Energy level diagram of the tunnel junction between a metal tip and metal surface. The left hand side of the figure represents a negatively biased sample, whereas the right hand side represents a positively biased sample. Electrons occupying states within the energy window ΔE can tunnel from the sample to the tip and from the tip to the sample, respectively. Φ_S and Φ_T are the barrier heights for the sample and tip, and z is the width of the tunnel gap.

which quantum particles (electrons) can penetrate a potential barrier or vacuum barrier. The tunneling probability, P , is given by

$$P \propto \exp(-2d\sqrt{2m(\Phi_0 - E)/\hbar^2}) \quad (2.13)$$

The tunneling effect has a solid theoretical foundation. For small tunnel voltage, the tunnel current is written as [Tersoff, 1985]

$$I = \frac{2\pi e}{\hbar} \sum_{\mu,\nu} f(E_\mu)[1 - f(E_\nu + eV)] |\mathbf{M}_{\mu\nu}|^2 \delta(E_\mu - E_\nu) \quad (2.14)$$

where $f(E)$ is the Fermi function, V the applied voltage, $M_{\mu\nu}$ is the tunneling matrix element, and E_μ and E_ν are the energies of states ψ_μ and ψ_ν in the absence of tunneling. The matrix element $M_{\mu\nu}$ is given by

$$\mathbf{M}_{\mu\nu} = \frac{\hbar^2}{2m} \int d\mathbf{S} \cdot (\psi_\mu^* \nabla \psi_\nu - \psi_\nu \nabla \psi_\mu^*). \quad (2.15)$$

The above equation originated from Bardeen's tunneling theory [Bardeen, 1961]. However, this formalism only applies to the cases of small voltage and low temperature. At elevated temperatures, an additional term for reverse tunneling should be added to the above equation showing influence of temperature and bias.

These theoretical expressions are often used in scanning tunneling spectroscopy (STS) experiments, which provide information about the local density of states. By varying the potential, difference between tip and sample at a fixed tip-sample separation, one can measure the $I(V)$ spectrum as well as the differential conductance $dI/dV(V/I)$ which directly reflects the local electronic density of states (LDOS).

When practicing STM, it is important to be aware of imaging artifacts. Figure 2.9 illustrates a double tip effect. In such a case, the current image represents the overlap of several images originating from the multiple protrusions at the apex of the tip. One might thus observe images with “ghosts”, resulting in unreasonable z -axis deflection.

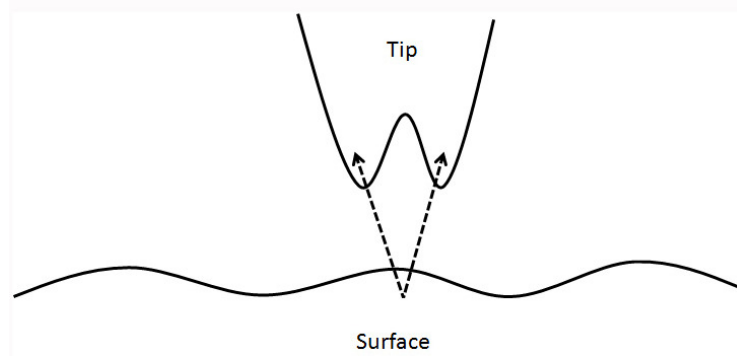


Figure 2.9
Sketch of a tip with two protrusions.

2.4. Superconducting Quantum Interference Device (SQUID) magnetometer

The Superconducting Quantum Interference Device (SQUID) is a Josephson junction device, which utilizes the phenomenon of superconducting phase coherence. It is the most sensitive device for detecting magnetic flux. The SQUID consists of a ring of superconducting material containing one or more thin insulating barriers or “weak links”. There are two main types of SQUID systems: radio frequency (rf) SQUID (or ac SQUID) with a single Josephson junction, and dc SQUID, which has several Josephson junctions. Figure 2.10 illustrates operation principles of dc SQUID. Electrons tunnel through the junctions so that supercurrent can flow around the loop through both Josephson junctions. The presence of a magnetic flux inside the loop in the normal direction causes a phase difference between electrons. The flux induces current around the loop. This potential difference across the loop can be measured. The transport supercurrent is

$$I_S = \left(\frac{I_C}{2}\right)(\sin \gamma_2 - \sin \gamma_1) \quad (2.16)$$

where I_C is the maximum supercurrent that the junction can support, and γ_1 and γ_2 are the phase differences across junctions indexed 1 and 2, respectively. The circulating supercurrent is constrained by

$$\gamma_1 - \gamma_2 = 2\pi\Phi/\Phi_0(\text{mod } 2\pi) \quad (2.17)$$

where $\Phi_0 \left(= \frac{2\pi\hbar}{2e} \cong 2.0678 \times 10^{-15} \text{ tesla} \cdot \text{m}^2\right)$ is a flux quantum, Φ the magnetic flux inside the loop.

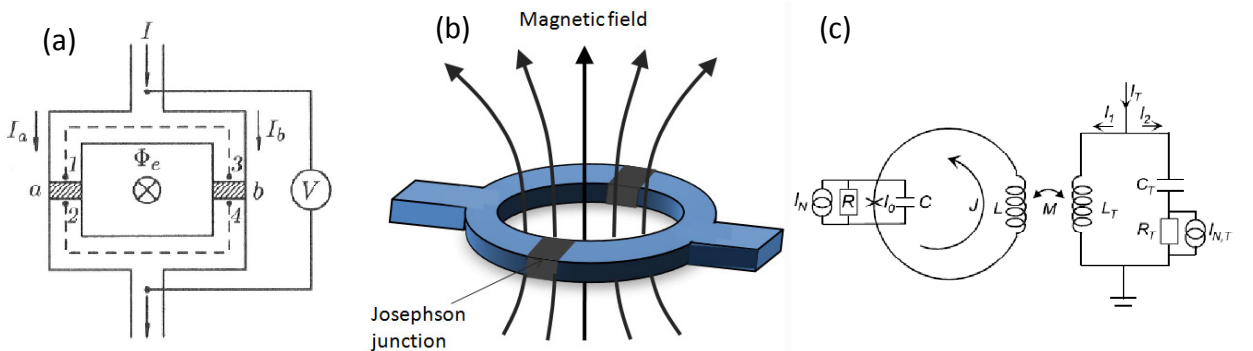


Figure 2.10

(a-b) dc SQUID. (c) The rf SQUID inductively coupled to its tank circuit.

An rf SQUID was used in the current experiment, as a detector in a Quantum Design model MPMS-XL magnetometer. The rf SQUID uses a radio frequency oscillating current (typically ~ 20 to 200 MHz) and measures interactions between the superconducting ring and an external circuit which consists of an inductor and a capacitor, forming a resonant LC circuit (Figure 2.10 (c)). The circulating current is

$$I_S = I_C \sin(2\pi\Phi/\Phi_0) \quad (2.18)$$

The phase difference across the weak link is given for the single-junction case by

$$\gamma = 2\pi\Phi/\Phi_0 \pmod{2\pi} \quad (2.19)$$

The rf signal in the LC circuit coupling to the loop depends periodically on the dc flux enclosed by the loop with period Φ_0 . The Q factor of the tank circuit (Figure 2.11) and the rf voltage are modulated by the rf loss. The detected rf voltage provides the flux-dependent output. This circuitry allows the SQUID to serve as an extremely sensitive detector of changes in magnetic flux (and hence electrical current). In practice, it is use as a null detector in a flux-locked loop, where as described below, the nulling voltage is a very large multiple of the change in flux or current.

Figure 2.11 (a) illustrates a detection coil which is connected to the input of a SQUID. This separate circuit is constructed entirely of superconductive wire and it serves as a “flux transformer.” When a magnetized material (a magnetic moment) moves through the coils, the changing magnetic flux in the detection coils induces a change in the current, which is measured by the SQUID. The second-order gradiometer shown in Figure 2.11 (a) is in Helmholtz geometry

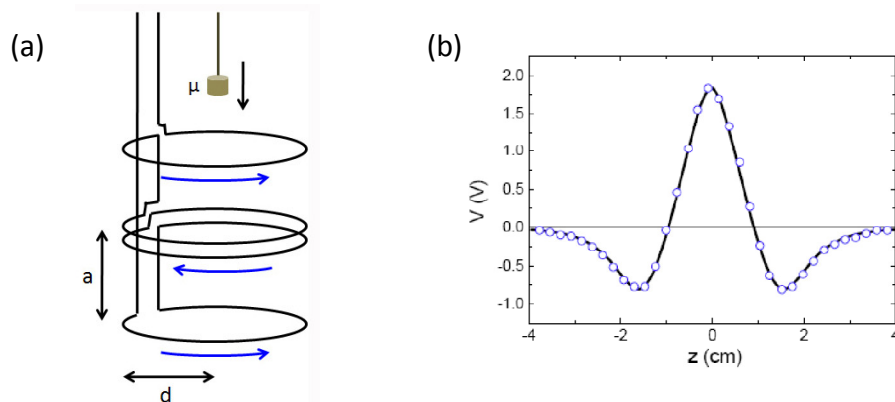


Figure 2.11

(a) A second-order gradiometer. (b) The magnetic flux induced by a dipole moving along the axis z of the coils generates a typical voltage reading from the pick-up coils.

($a = 2d$). When the sample moves through the pick-up coil, the magnetic moment of a sample is determined by the measured output voltage from the SQUID electronics. The output voltage variation of the SQUID is proportional to the total magnetic flux change in the position-dependent output signal $V(z)$. In Figure 2.11 (b), the side peaks in $\Phi(z)$ do not coincide precisely with the positions of the external coils.

2.5. Interface reconstruction

Semiconductor surfaces and interfaces have physical and chemical properties that are very different from the bulk. When a semiconductor crystal such as silicon is cleaved in ultrahigh vacuum, surface atoms lose their tetrahedral coordination and will try to compensate for this loss of bonding by forming new bonds. Accordingly, the surface “reconstructs” and this reconstructed surface is likely to have new properties. When another species is deposited onto a reconstructed surface, the surface is likely to change its structure again. In this section, we will briefly review the properties of the clean Si(111)- 7×7 surface reconstruction and discuss the structural transformations that take place when a metal element such as Ga or Pb is deposited onto this structure. The resulting structures are usually referred to as Si(111)- $\sqrt{3} \times \sqrt{3}$ -R30°-M reconstructions where M is the metallic element. This background information will be needed for our discussion in Chapters 4 and 5.

2.5.1. *Si(111)- 7×7 surfaces*

Bulk silicon has the diamond structure in which all atoms are tetrahedrally bonded to four neighboring atoms. When a Si(111) surface is cleaned in ultrahigh vacuum, for instance by thermal flashing or annealing of an out-of-the-box wafer at about 900 °C, the surface adopts a very complicated structure with a translational period that is seven times larger than that of the primitive hexagonal unit cell in the bulk truncated (111) plane. The surface thus exhibits a (7×7) super-period, hence the notation Si(111)- 7×7 . The existence of this reconstruction is evident from the beautiful LEED patterns, showing many satellite diffraction spots (Figure 2.12(a)), and from the STM images (Figure 2.12(b)).

The Si(111)- 7×7 structure or “Dimer Adatom Stacking-fault (DAS) reconstruction” consists of two triangular subunits constituting the “faulted” and “unfaulted” half of the (7×7) supercell (Figure 2.12(a)). The faulted subunit is created by a stacking fault in the underlying Si layer. The

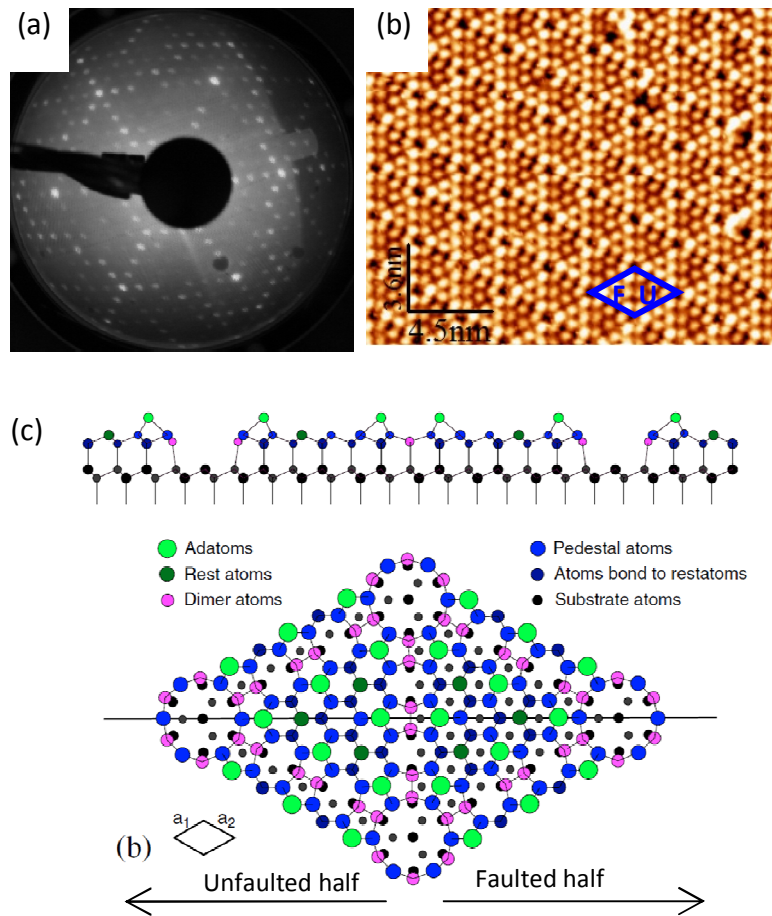


Figure 2.12

(a) LEED pattern (70 eV) and (b) STM image of the Si(111)- 7×7 surface. (c) The dimer-adatom-staking fault (DAS) model by Takayanagi et al [Takayanagi, 1985]. Side view: atoms in the lattice plane along the long diagonal of the surface unit cell are shown with larger circles than those behind them. Top view: atoms in (111) layers at increasing depth are indicated by circles of decreasing sizes. The green circles represent the 12 adatoms per unit cell, and the 6 rest atoms are shown as dark green circles. The right half of the unit cell contains the stacking fault.

faulted and unfaulted units are connected by a (7×7) network of Si-Si dimers [Takayanagi, 1987]. The faulted and unfaulted half are furthermore decorated with a total of 12 Si adatoms. Each adatom ties up three dangling bonds by forming so-called backbonds but at the same time, each adatom also introduces a new dangling bond. The structure is furthermore characterized by deep “corner holes” at the vertices of the (7×7) dimer network. These holes are a key characteristic of the STM images. The bright blobs in these images correspond to the Si adatoms whereas the dark holes indeed correspond to the corner holes. Finally, there are six “restatoms” in the second layer, contributing one dangling bond each. Because they are one layer down, they are not easily seen with STM.

The (7×7) reconstruction is a remarkable demonstration of nature’s creativity in reducing the number of costly dangling bonds. Without reconstruction, a (7×7) supercell would have 49 atoms with 49 half-filled dangling bonds. After reconstruction, there are only 19 dangling bonds left: 12 on the adatoms, 6 on the restatoms and 1 in the corner hole. The dangling bonds on the restatom and corner hole are located below the outermost adatom layer and acquire double occupancy by “stealing” a total of seven electrons from the adatoms. In all, the number of unpaired electrons per unit cell has been reduced from 49 to 5. These electrons are localized on the adatoms. The odd electron count suggests that the Si(111)- 7×7 surface might be metallic. This is indeed the case: the surface of a semiconductor can be metallic [Losio, 2000].

One might naively assume that all (111) surfaces would form such amazing reconstructions. However, reconstructions like the (7×7) surface also contain many strained bond angles. The total energy minimized structure is the result of a delicate balance between the electronic energy gain associated with the reduction of dangling bonds and the energy penalty incurred by the straining of bond angles (the “ideal” bond angle is 109°). The outcome is difficult to predict. For instance, the Ge(111) surface reconstruction is entirely different. However, the observation of DAS reconstructions on a strained Ge layer grown on Si(111) demonstrates the important role of surface stress in the reconstruction.

2.5.2. *Si(111)- $\sqrt{3} \times \sqrt{3}$ R30-M surfaces*

Submonolayer amounts of metal atoms such as Ga or Pb easily destroy the (7×7) reconstruction (provided that enough thermal activation energy is being supplied), leading to the formation of a new superstructure. A very common metal-induced reconstruction on Si(111) is the $(\sqrt{3} \times \sqrt{3})$ -R30° reconstruction. The unit cell has tripled in size, compared to the primitive unit

cell in the Si(111) plane, and is rotated by 30° . Figure 2.13(a) shows the LEED pattern of the Si(111)- $\sqrt{3} \times \sqrt{3}$ -R30°-Ga reconstruction revealing the $(\sqrt{3} \times \sqrt{3})$ -R30° superlattice diffraction spots. Figure 2.13(b) displays an STM image of this surface at room temperature.

The surface layer of Si(111) has several high-symmetry locations (“sites”) for atoms to adsorb. The primary sites are T_1 , T_4 , and H_3 . The T_1 site is an adsorption-site right on *top* of a first-layer Si atom, see Figure 2.14(a). The H_3 site is a 3-fold coordinated adsorption site in the hollow created by first- and second-layer Si atoms, and is located above a fourth-layer Si atom (Figure 2.14(b)). The T_4 site is a 4-fold coordinated adsorption-site on *top* of a second-layer Si atom (Figure 2.14(c)). Note that all of these special chemisorption sites form a $(\sqrt{3} \times \sqrt{3})$ -R30° superlattice. If the T_4 or H_3 chemisorption sites were all occupied, the metal coverage would be exactly 1/3 ML.

In many cases, it is not clear which chemisorption site is favored. However, the chemisorption site can be determined experimentally by studying domain boundaries between the (7×7) and $(\sqrt{3} \times \sqrt{3})$ -R30° reconstructions on an underdosed surface. Because the registry of the adatoms on the (7×7) surface is known (T_4), one can determine the chemisorption site on the neighboring $(\sqrt{3} \times \sqrt{3})$ -R30° structure from the lateral registry of the adatoms (Figure 2.14(e)).

2.5.3. “Devil’s staircase” ($1.2 < \theta < 1.3$ ML)

To calibrate the deposition rate of Pb, we exploit the fact that the phase diagram of Pb on Si(111) exhibits many different phases with precisely known adatom densities (Figure 2.15 (a)).

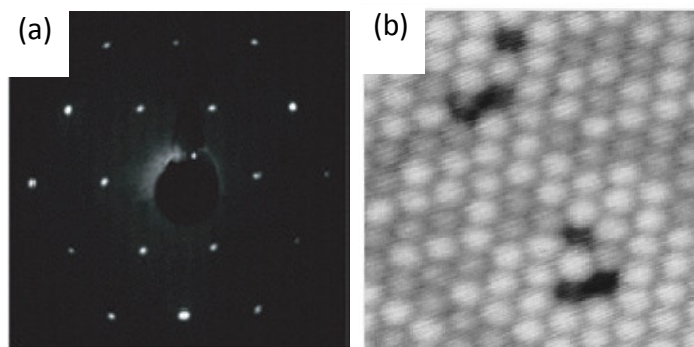


Figure 2.13

(a) LEED pattern (55 eV) (Image from [Čechal, 2007]) and (b) STM image (7×7 nm²) (+2V) (Image from [Hibino, 1996]) of the Si(111)- $\sqrt{3} \times \sqrt{3}$ -R30°-Ga surface. The Ga coverage is 1/3 ML.

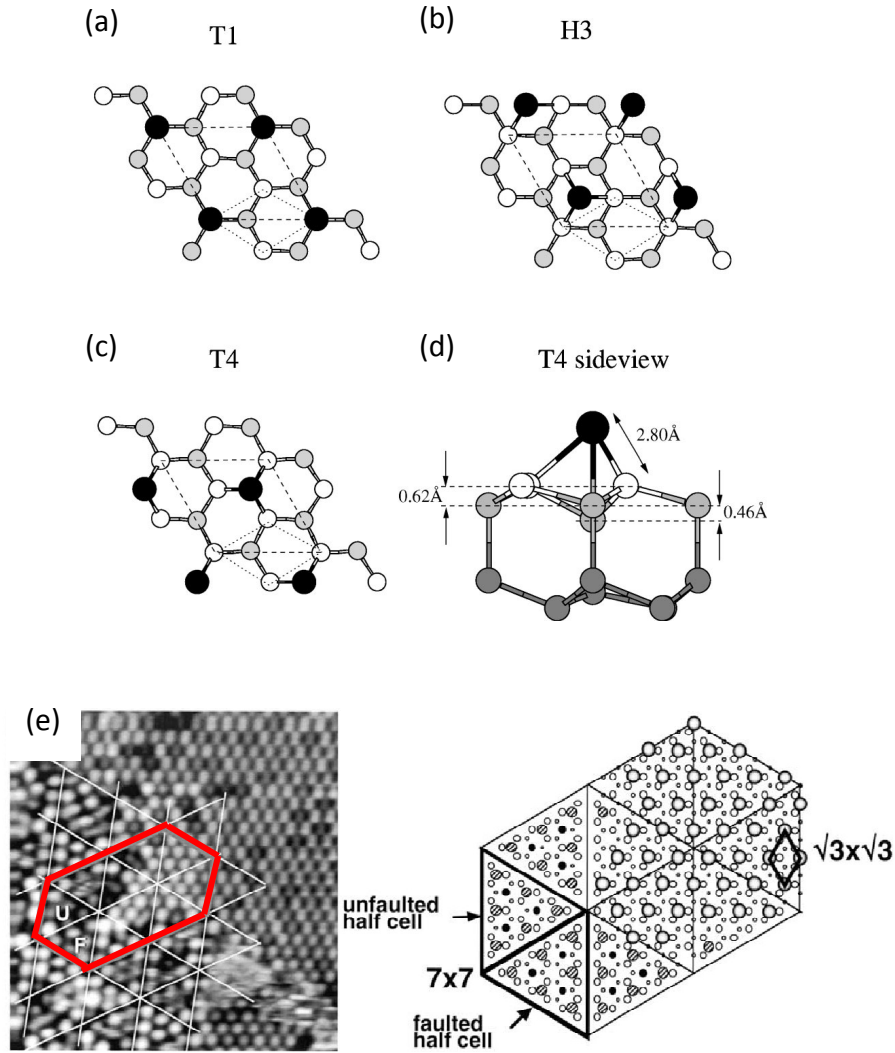


Figure 2.14

(a) T₁ model, (b) H₃ model, (c) T₄ model, and (d) side view of the T₄ model for the 1/3-ML phase. Chemisorbed adatoms are shown in black. Si atoms in the first and second layer below the adatoms are shown in white and gray, respectively. Only the first two layers of the Si substrate are shown in the top view illustrations. For the side view illustration, the top four layers of the Si substrate are shown. The 1 × 1 unit cell is indicated by dotted lines and the ($\sqrt{3} \times \sqrt{3}$) unit cell is indicated by dashed lines. The top view and the side view are not drawn at the same scale (Image from [Chan, 2003]). (e) STM images containing mixed domains of Si(111)- $\sqrt{3} \times \sqrt{3}$ -R30°-Pb and Si(111)-7 × 7, recorded at a sample bias of - 0.5 V. A schematic illustration of the area inside the red hexagon is shown on the right side.

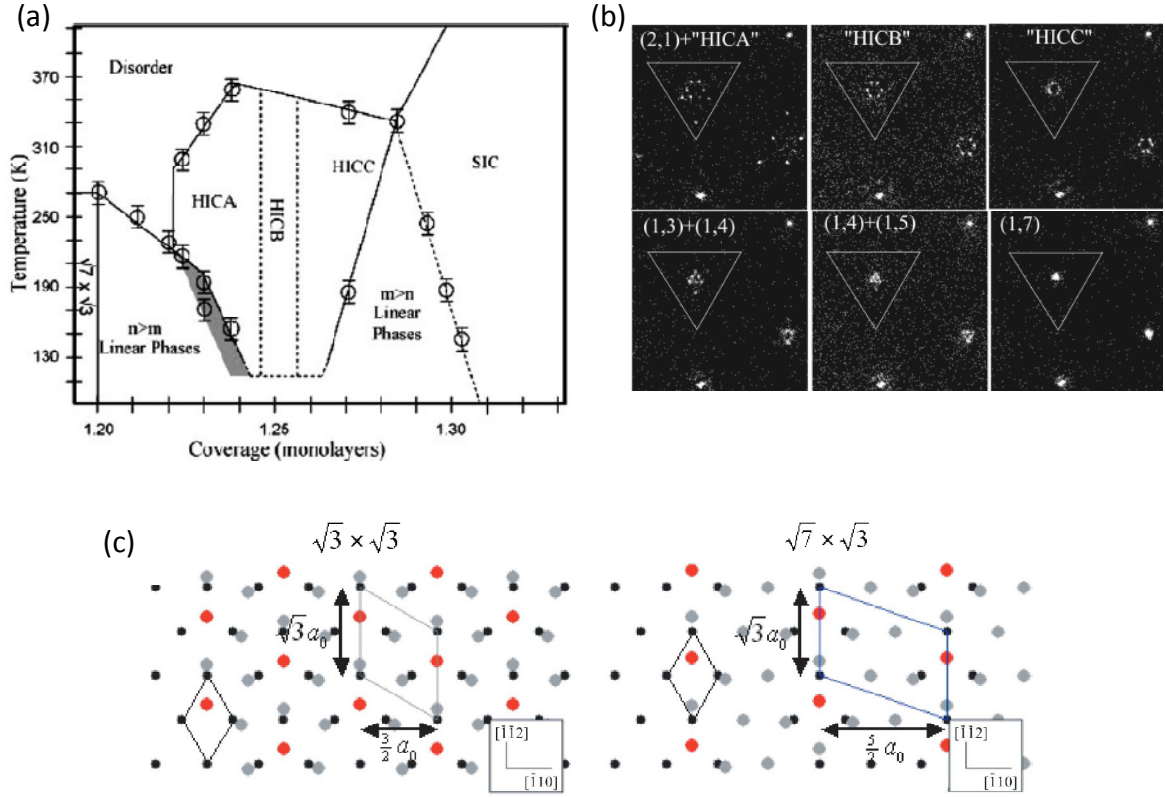


Figure 2.15

(a) Phase diagram of a monatomic Pb layer on Si(111) in the coverage range $1.2 \text{ ML} < \theta < 1.33 \text{ ML}$ (Image from [Stepanovsky, 2006]). (b) Corresponding LEED patterns. Stepwise deposition experiments at constant temperature ($\sim 169 \text{ K}$) reveal the formation of the various (n, m) commensurate phases following the Devil's Staircase hierarchy. (c) Schematic model of the $(\sqrt{3} \times \sqrt{3})$ and $(\sqrt{7} \times \sqrt{3})$ structures. Pb atoms at high symmetry positions (H_3) are shown in red.

For instance, a monatomic Pb layer on Si(111) exhibits up to 12 commensurate phases within the narrow coverage range $6/5 \text{ ML} < \theta < 4/3 \text{ ML}$. The lower limit density is equivalent to the atomic density of a (111) layer in bulk Pb. The upper limit density is equivalent to that of a 5%-compressed Pb(111) layer. The existence of these phases is indicated by the LEED patterns in Figure 2.15(b). The (n, m) commensurate phases can be generated from $n(\sqrt{7} \times \sqrt{3})$ ($\theta = 1.2 \text{ ML}$) and $m(\sqrt{3} \times \sqrt{3})$ ($\theta = 1.33 \text{ ML}$) unit cells, following the combinatorial rules of a "Devil's staircase" [Bak, 1987; Hupalo, 2003; Yakes, 2004]. A schematic illustration of these two 'generating phases' is shown in Figure 2.15(c). The $(\sqrt{3} \times \sqrt{3})$ unit cell has four Pb atoms, three of them are located at off-centered T_1 sites and one atom is located at the H_3 site. The unit cell of the $(\sqrt{7} \times \sqrt{3})$ phase

contains six Pb atoms; five of them are located at off-centered T_1 sites and one is located at the H_3 site.

In the phase diagram of Figure 2.15(a), HIC stands for the “hexagonal-incommensurate” phase and SIC for the “striped-incommensurate” phase. This nomenclature is historical but unfortunately incorrect. It turns out that the HIC and SIC phases are in fact commensurate phases with large unit cells. The evolution of each phase with varying coverage is easily followed with LEED, as shown in Figure 2.15(b). As the coverage inches closer to $4/3$ ML, the clusters of superlattice spots merge into a sharp diffraction spot at the commensurate $(\overline{1/3}, \overline{1/3})$ positions.

In our coverage calibration experiment, we deposited a single layer of Pb onto Si(111)- 7×7 at 250 °C. This removes the (7×7) reconstruction and ensures proper equilibration. Excess Pb evaporates at this temperature [Reedijk, 2003; Hupalo, 2003]. After cooling to room temperature, we recorded the LEED pattern. We observed a sharp $(\sqrt{3} \times \sqrt{3})$ LEED pattern similar to that of the $(1, 7)$ phase in Figure 2.15(b). This indicates that the coverage at the kink position in Figure 2.3 is 1.3 ML.

CHAPTER 3

Controlled Self-organization of Atom Vacancies in Monatomic Gallium Layers

Ga adsorption on the Si(112) surface results in the formation of pseudomorphic Ga atom chains. Compressive strain in these atom chains is relieved via creation of adatom vacancies and their self-organization into meandering vacancy lines. The average spacing between these line defects can be controlled, within limits, by adjusting the chemical potential μ of the Ga adatoms. We derive a lattice model that quantitatively connects density functional theory (DFT) calculations for perfectly ordered structures with the fluctuating disorder seen in experiment and the experimental control parameter μ . This hybrid approach of lattice modeling and DFT can be applied to other examples of line defects in heteroepitaxy.

3.1. Introduction

Many physical, chemical, and biological phenomena are manifestations of self-organization of matter, such as crystal growth, protein folding, or formation of galaxy clusters. Well-known examples of self-organization in advanced materials systems include the formation of magic metal clusters, pyramid quantum dots, quantum dot superlattices in heterostructures [Springholz, 1998; Brune, 1998], and the ordering of atom vacancies into line defects or vacancy line superstructures [Liu, 1997; Voigtländer, 2001; Chen, 1994]. For application purposes, it would be essential to control the size, uniformity, and spacing of such nano-objects. This goes against the odds of thermodynamic fluctuations that are especially profound in low-dimensional systems, and the stochastic nature of nucleation and growth.

In this Chapter, we show that the average spacing between vacancy lines in a monatomic Ga layer on Si(112) can be controlled and varied continuously, within limits, via the chemical potential of the adsorbate species, μ . Ga vacancies self-organize into a $n \times 1$ vacancy line superstructure (see Figures 3.1(a-c)), similar to the formation of the well-known $n \times 2$ superstructures for Ge on Si(100) [Erwin, 1999; Liu, 1997; Voigtländer, 2001; Chen, 1994]. Entropic fluctuations compete with this ordering process, however, resulting in meandering vacancy lines where the average line spacing is fixed by the chemical potential. The meandering amplitude is limited by elastic repulsions between vacancy lines. Such a two-dimensional interacting vacancy line system has been modeled as a one-dimensional random walker trapped in a harmonic potential representing the collective mean field of all the other vacancy lines [Chen, 1994]. For systems such as Ge on Si(100), this one-dimensional model seems to capture the observed meandering quite well, allowing for a straightforward determination of the kink energy and line repulsion from statistical analysis of fluctuations in Scanning Tunneling Microscopy (STM) images. Step fluctuations on vicinal crystal surfaces have been analyzed in similar fashion, using continuum modeling [Bartelt, 1992].

An interesting question is how the constraints imposed by the discreteness of a lattice modifies the elastic interactions that are driving the self-organization of vacancies, particularly for short vacancy line spacings. Discrete vacancy line spacings conceivably lead to significant vacancy-vacancy correlations that cannot be captured by the usual mean field or continuum models. Ga on Si(112) turns out to be an interesting test case. By tuning the average line spacing between $n = 5$ and $n = 6$ (see Figure 3.1) we find that the discrete distribution of vacancy line

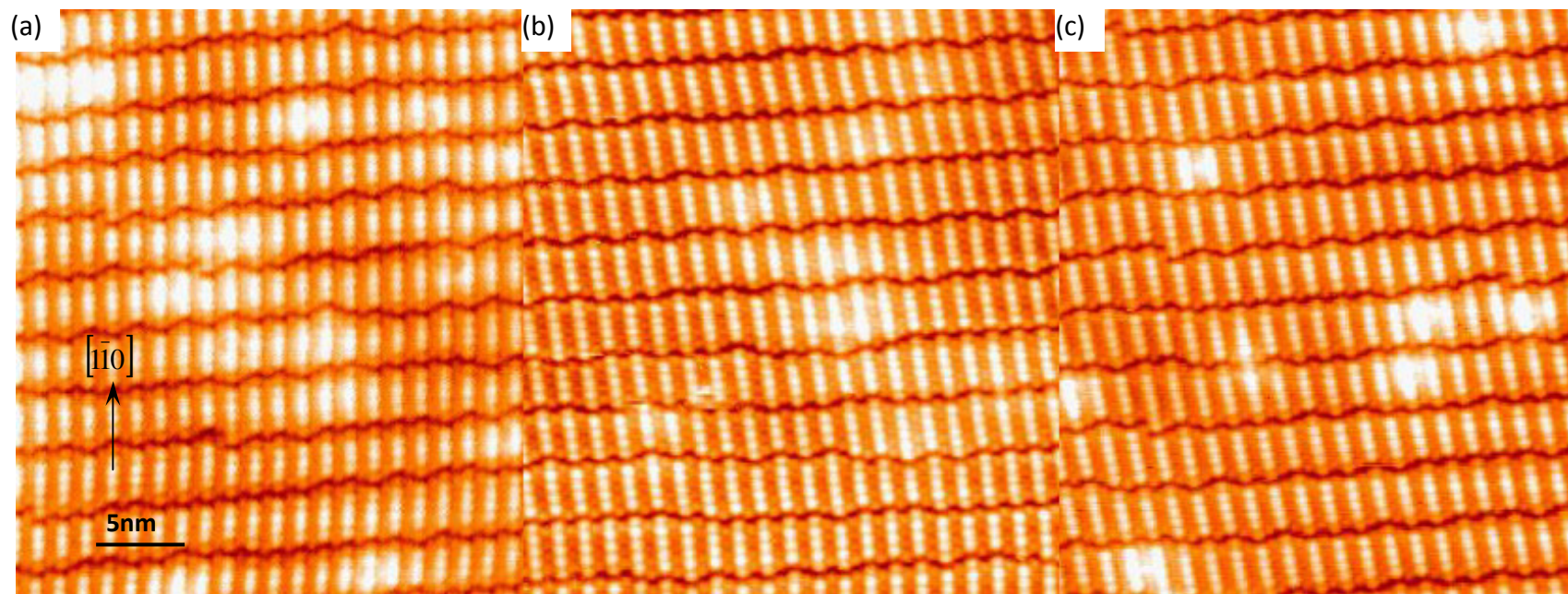


Figure 3.1

STM images of the Ga-covered Si(112) $n \times 1$ surface: (a) $n = 5.49$, (b) $n = 5.68$, and (c) $n = 5.88$.

spacings does not follow the scaling behavior predicted by the mean field model, and that correlations cannot be ignored. Guided by our experimental observations, our theory collaborators at the Autonomous University in Madrid constructed a lattice model in which the surface is represented as an entropic mixture or solid solution of different $m \times 1$ building blocks (henceforth m will be reserved for integers and n for the average periodicity). The model naturally takes into account the discrete nature of the vacancy line spacing and contains only two parameters: (1) the chemical potential of the adsorbate which can be varied experimentally; and (2) the repulsive interaction between vacancy lines, which our collaborators calculated from density functional theory (DFT) and which we verified experimentally. The lattice model connects the DFT results, calculated for perfect order, with the fluctuating disorder seen in experiment.

3.2. Experimental Procedures

Experiments were carried out in ultrahigh vacuum, employing STM and low energy electron diffraction (LEED). Detailed experimental procedures for obtaining the Ga/Si(112)- $n \times 1$ surface reconstruction have been reported elsewhere [González, 2004; Snijders, 2005]. The $n \times 1$ periodicity was controlled by adjusting the Ga flux. All samples were equilibrated at 810 K for about 15 minutes and subsequently cooled to room temperature at ~ 2 K/sec. Theoretically, within our local orbital DFT calculation (see below), the 6×1 structure is stable for $-0.6 < \mu < -0.2$ eV while the 5×1 structure is stable below -0.6 eV ($\mu_{\text{bulk}} \equiv 0$). μ can be estimated from $\mu = \mu_{\text{bulk}} - kT \ln(p_c/p_s)$, where p_c and p_s are the Ga vapor pressures inside the effusion cell and at the sample, respectively [González, 2004; Snijders, 2005].

3.3. Results and Discussions

Figures 3.1(a-c) show three large-scale empty state STM images of the Si(112)- $n \times 1$ -Ga surface, obtained at different μ . Dark vacancy lines meander perpendicular to the Ga adatom rows [González, 2004; Snijders, 2005]. From these images, we identified several $m \times 1$ unit cells where ma is the spacing between neighboring Ga vacancies along the $[1\bar{1}0]$ direction ($a = 0.384$ nm is the lattice constant). A row of Ga atoms is adsorbed at the (111)-like step-edge sites of the Si(112) surface, while a second row of Ga atoms is adsorbed on the terrace sites (see Figures 3.2(a) and

(b)) [González, 2004; Snijders, 2005]. The resulting zigzag chains are interrupted by the meandering vacancy lines. For each $m \times 1$ unit cell, there are $m \times 1$ Ga atoms on the terrace sites whereas the number of step-edge Ga atoms fluctuates between $m \times 2$ and m [González, 2004; Snijders, 2005]. Therefore, in order to acquire statistical information on the distribution of unit cell sizes, one needs to collect large-scale images and count the number of terrace atoms within each unit cell. This was most easily accomplished using empty state images.

The probability distributions of the $m \times 1$ unit cells from these images are shown in Figure 3.3 for different average periodicities with $5 < n < 6$ (i.e., different μ). A typical sample image contained about 2000 unit cells. The vast majority of unit cells are either 5×1 or 6×1 with a small percentage of 4×1 and 7×1 unit cells. As shown, the experimental distributions can be fitted to Gaussian distribution functions with great accuracy. The Gaussian widths are practically constant ($\sigma = 0.49 \pm 0.02$) for the indicated values of n , conflicting with the 13% change predicted by the continuum model [Chen, 1994; Bartelt, 1992].

Figure 3.4 shows the LEED line profiles along the $[1\bar{1}0]$ direction for various μ (and thus various n). The fractional order spots are incommensurate with the integer order reflections and shift continuously with μ . They can only be indexed with three indices, instead of the two usual (h, k) Miller indices, $\vec{q} = \left(h \pm \frac{p}{n}\right) \vec{a} + k \vec{b}^*$, where $\vec{a}$ and $\vec{b}^*$ are the reciprocal lattice vectors parallel and perpendicular to the Ga chains, respectively, and $\vec{q}$ is the momentum transfer. The fractional number n represents the average vacancy line spacing (see below) and p is an integer. Evidently,

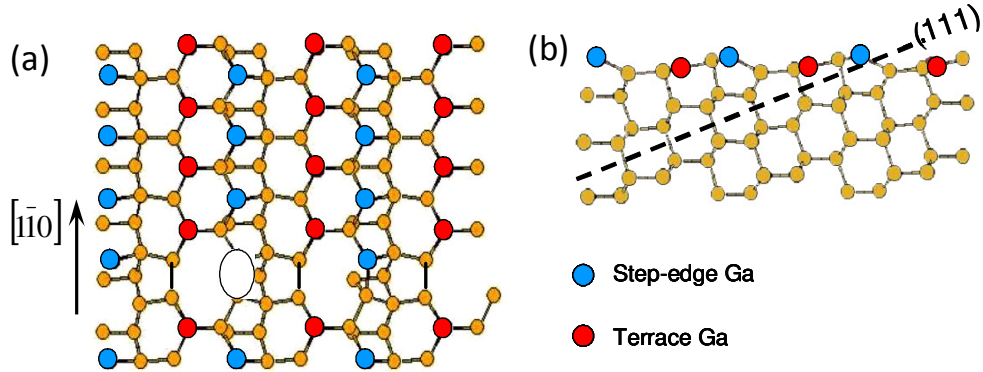


Figure 3.2

(a) Top view and (b) side view of a ball and stick representation of the Si(112)- 6×1 -Ga surface. (Figure from ref [González, 2004])

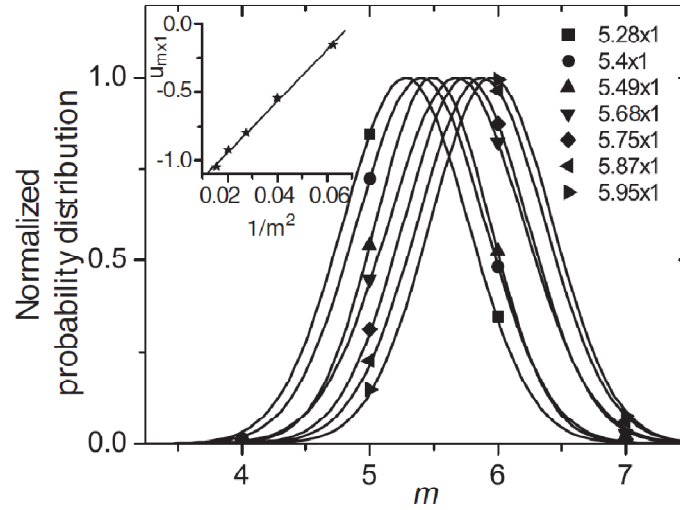


Figure 3.3

Normalized distributions of $m \times 1$ unit cells on the surface, fitted with Gaussians. The centroid of Gaussian distribution shifts from $n = 5.28$ to $n = 5.95$ with increasing μ . Their standard deviations are $\sigma = 0.49 \pm 0.02$. Inset: $u_{m \times 1}$ [in eV; see Eq. (1)] versus $1/m^2$ for $m = 4, 5, 6, 7$, and 8 from DFT calculations for $\mu = -0.55$ eV.

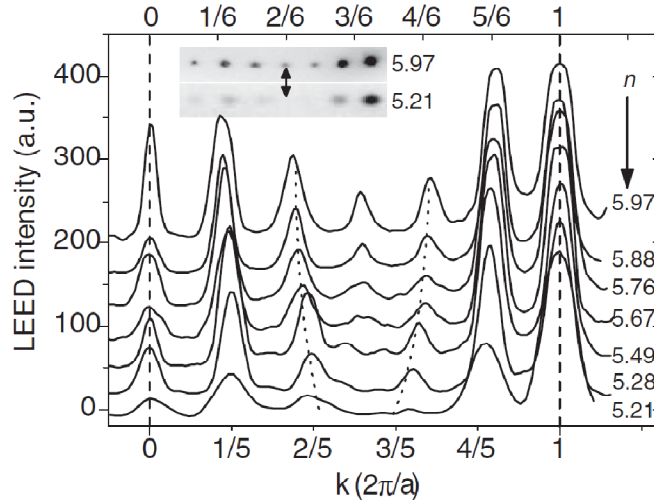


Figure 3.4

LEED intensity profiles of the Ga-covered Si(112)- $n \times 1$ surface (70 eV). The average $n \times 1$ periodicities determined from the intensity profiles are indicated on the right. Dotted lines follow the continuous shifts of the fractional order spots. Inset: sections of the LEED image for $n = 5.97$ and $n = 5.21$.

varying amounts of Ga on the surface result in an entropic mixture of 5×1 and 6×1 units. This is consistent with an autocorrelation analysis of the vacancy line pattern in the STM image (not shown) that shows that the sequence of 5×1 and 6×1 units along the $[1\bar{1}0]$ direction is random. Indeed, the periodicity from LEED coincides with the centroids of the Gaussian fits in Figure 3.3 to within 1%.

Next, we analyze the distribution of unit cells in the surface by combining DFT calculations with a one-dimensional lattice model. First, we analyze the interaction between vacancy lines via DFT–local-density approximation (DFT-LDA) total energy calculations, for different periodic $m \times 1$ reconstructions ($m = 4, 5, 6, 7$ or 8). From these calculations, $u_{m \times 1} = (e_{m \times 1} - 2(m - 1)\mu) - (me_{1 \times 1} - 2m\mu) = e_{m \times 1} - me_{1 \times 1} + 2\mu$, where $e_{1 \times 1}$ is the total energy for a 1×1 unit cell (surface without vacancy lines). Thus we obtain $u_{m \times 1} \equiv \Delta(e_{m \times 1} - n_{\text{Ga}}\mu)$, where $e_{m \times 1}$ is total energy per $m \times 1$ unit cell, and $n_{\text{Ga}} = 2(m - 1)$ the number of Ga atoms per $m \times 1$ unit cell. The variation Δ is taken with respect to a hypothetical surface without vacancy lines. We used an efficient local orbital DFT-LDA code [Demkov, 1995]. The use of a local orbital approach guarantees that the basis set is strictly the same in the different calculations. In addition to this, the DFT analyses are based on total-energy comparisons for different periodicities. Similar calculations using a plane-wave code would require very large basis sets because the cancellation of errors implicit in the calculation of total-energy differences is only effective when comparing calculations with identical basis sets. The inset of Figure 3.3 shows $u_{m \times 1}$ plotted as a function of $1/m^2$. The straight line indicates that the repulsive interaction between vacancy lines is elastic in nature [Marchenko, 1980; Zandvliet, 2000]. Accordingly [Ciobanu, 2004]:

$$u_{m \times 1} = \Lambda + G/m^2 \quad (3.1)$$

where G defines the repulsive interaction between vacancy lines and Λ is the formation energy per unit cell of a vacancy line that implicitly depends on μ as $\Lambda = \Omega + 2\mu$ (there are two Ga vacancies per unit cell), where Ω is a constant. From the slope of $u_{m \times 1}$ versus $1/m^2$, we obtain $G = 19 \pm 1$ eV.

In a second step we introduce a one-dimensional lattice model in which the surface is considered as an entropic mixture of different $m \times 1$ unit cells, thus neglecting the two-dimensional meandering along the vacancy lines. The following analysis of the vacancy line interactions and kink energy is conceptually different from the mean field analysis in, e.g., Ref. [Chen, 1994], which described the meandering of an individual vacancy line in a mean field

potential as a function of the kink energy. Here, we derive a unit cell distribution by considering an ensemble of straight lines with no kinks. Kinks are analyzed separately without reliance on a mean field model.

In our lattice model, the vacancy lines are straight lines and the system is characterized by the numbers N_m ($m = 4, 5, 6, 7$) representing the number of 4×1 , 5×1 , 6×1 , and 7×1 unit cells of the system, and the number of vacancy lines is $N = N_4 + N_5 + N_6 + N_7$. According to our previous discussion, we write for this one-dimensional model:

$$U \equiv \Delta(E - \mu N_{Ga}) = N\Lambda + \sum_m N_m G / m^2 \quad (3.2)$$

where E is the total energy of the surface and $N_{Ga} = 6N_4 + 8N_5 + 10N_6 + 12N_7$ the number of Ga atoms on the surface. We can define the following partition function

$$Z = \left(\frac{N!}{N_4! N_5! N_6! N_7!} \right) \exp \left(- \frac{E - \mu N_{Ga}}{kT} \right) \quad (3.3)$$

and maximize Z with the condition that $M = 4N_4 + 5N_5 + 6N_6 + 7N_7$ is constant (i.e., the size of the system is fixed). This yields a set of equations that give $n_m = N_m/N$ as a function of μ and T :

$$\ln[n_5^4/n_4^5] = (\Lambda + (1/4^2 + 1/(4 \times 5) + 1/5^2)G) / kT \quad (3.4)$$

$$\ln[n_6^5/n_5^6] = (\Lambda + (1/5^2 + 1/(5 \times 6) + 1/6^2)G) / kT \quad (3.5)$$

$$\ln[n_7^6/n_6^7] = (\Lambda + (1/6^2 + 1/(6 \times 7) + 1/7^2)G) / kT \quad (3.6)$$

The numerator on the right hand side of these equations is related to $u_{m \times 1}$ for the different $m \times 1$ periodic reconstructions. For example, $6u_{5 \times 1} - 5u_{6 \times 1}$ obtained via Eq. (3.1) equals the numerator on the right in Eq. (3.5). This result allows us to make a direct connection between the lattice model, Eqs. (3.4)–(3.6), and the DFT-LDA calculations performed for $u_{m \times 1}$.

Eqs (3.4)–(3.6) represent near-perfect Gaussians, showing only a marginal skewness to high n ; this is most clearly found near $n = 5.5$. Direct data fitting to Eqs. (3.4)–(3.6) is unreliable because the tail of the distribution only consists of one data point, n_4 or n_7 ; both are subject to large statistical fluctuations. Therefore, motivated by the experimental observations, we first fitted Eqs. (3.4)–(3.6) to Gaussian distributions (see Figure 3.3) and then compared the widths of the theoretical Gaussians to the experimental ones. This produces an analytical expression that relates σ to G/kT ; μ drops out. We then find that $G/kT = 570 \pm 100$.

The relevant temperature is the temperature T_F below which the distribution is frozen. T_F can be estimated from the temperature variation of the LEED line profiles. We observed a significant narrowing of the LEED line profile above 500 K, indicating that spatial fluctuations start to randomize within the transfer width of the LEED system. This sets the upper limit for the freezing temperature. The lower limit is the temperature at which the STM data were recorded, i.e., room temperature. Accordingly, We thus estimate that $T_F \approx 400 \pm 100$ K. Using this value for T_F together with our LDA result for G ($G = 19 \pm 1$ eV), we obtain $G/kT = 550 \pm 170$, in good agreement with the value obtained above from the fitting to Eqs. (3.4)–(3.6). From the fitting, we find that the width of the distribution depends only on the ratio G/kT whereas the average periodicity depends on both G/kT and μ . Specifically, μ varies by 0.32 ± 0.08 eV for $5.21 \leq n \leq 5.95$, in good agreement with our local orbital calculations showing a variation in μ of 0.26 eV.

We finally turn our attention to the tw-dimensional meandering behavior and determination of the kink energy. We restrict our analysis to the case $n = 5.49$: in this case the surface contains almost equal amounts of 5×1 or 6×1 unit cells, with a negligible number of 4×1 and 7×1 unit cells (out of $N = 3461$ unit cells analyzed we found only six 4×1 and five 7×1 unit cells), and will be neglected in the following analysis.

A vacancy can be located in between a 5×1 and 6×1 unit cells, a configuration which we denote as 5 and 6 ; other configurations are $\frac{6}{5}$, $\frac{6}{6}$ and $\frac{5}{5}$. Similarly, the kinks in the vacancy lines can be classified according to the configuration of the four surrounding unit cells, as, e.g., $\frac{6}{5} \frac{5}{6}$ (Figure 3.5(a)), or $\frac{6}{6} \frac{6}{6}$ (Figure 3.5(b)), etc. Only kinks of the type $\frac{6}{5} \frac{5}{6}$ or $\frac{5}{6} \frac{6}{5}$ appear as regular kinks: all other kink configurations imply the presence of a correlated kink in a neighboring vacancy line, as indicated by the circles in Figure 3.5(b). Thus, we use the terms regular kink, to refer to $\frac{6}{5} \frac{5}{6}$ or $\frac{5}{6} \frac{6}{5}$ kinks, and nonregular kink for the others. Experimentally, we counted the total number of kinks, N_K , as well as the number of regular N_R and nonregular N_{NR} kinks, obtaining $N_K/N = 0.060$ and $N_{NR}/N_R = 0.20$. If all kinks were created independently, as implicitly assumed in mean field models of vacancy lines [Chen, 1994], then the ratio N_{NR}/N_R should have been 0.13 for the present case with $N_K/N = 0.06$. The $\sim 50\%$ higher fraction of nonregular kinks observed here implies correlated meandering, meaning that kink energies cannot be calculated reliably using the mean field model [Chen, 1994].

Based on the experimentally observed absence of ordering of the different $m \times 1$ unit cells in the $[1\bar{1}0]$ direction, our theory colleagues analyzed the number of one-step kinks, N_K , along a vacancy line using the model system depicted in Figures 3.5(c) and (d). In this model system of $4 \times 2 = 8$ unit-cells, we consider all $2^8 = 256$ possible configurations of 5×1 and 6×1 unit cells; the probability of each is proportional to $\exp(-n_k e_k / kT_F)$ where n_k is the number of kinks it contains and e_k the kink energy. We find that the ratios N_K/N and N_{NR}/N_R are already converged for this small-size model system. From this model we obtain N_K/N as a function of $\exp(-e_k/kT_F)$, and deduce the kink energy e_k using the experimental ratio $N_K/N = 0.06$ and $T_F = 400$ K. This yields $e_k = 73 \pm 20$ meV. From this model we can also obtain N_{NR}/N_R as a function of $\exp(-e_k/kT_F)$, and obtain an independent estimate of the kink energy. This procedure yields $e_k = 68 \pm 20$ meV, showing the consistency of this analysis (the errors mainly arise from the large uncertainty in T_F).

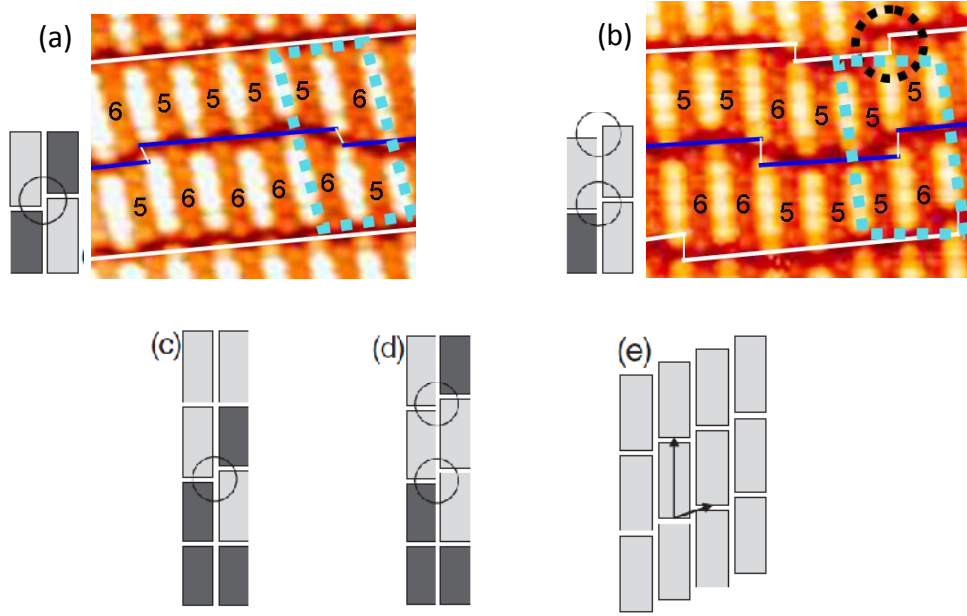


Figure 3.5

Schematic drawing of different kink configurations. Light / dark rectangles represent 6×1 / 5×1 unit cells. (a) *Regular* kink, (b) *nonregular* kinks (see text). (c) and (d) Two possible configurations for the model system used in our analysis. Circles in (a)–(d) highlight kink positions. (e) shows a portion of the oblique lattice used in the DFT calculations of the kink energy (oblique lattice vectors indicated by arrows).

We also estimated the kink energy e_k by means of DFT calculations for a periodic 6×1 and 5×1 arrangement of kinks using oblique lattice vectors; see Figure 3.5(e). These calculations yield $e_k = 80 \pm 10$ meV and $e_k = 88 \pm 10$ meV, respectively, in excellent agreement with the experimental values above. Note that a mean field analysis using $N_K/N = 0.06$ would have produced a higher kink energy of 119 ± 30 meV. This overestimation is consistent with the fact that vacancy correlations are not included in the one-dimensional mean field model, although they effectively suppress thermal meandering.

3.4. Summary

The self-organization process of atom vacancies in the Ga/Si(112) interface can be experimentally controlled via the chemical potential of the adsorbate. A new lattice model accurately connects first principles DFT calculations for ordered structures with experimental data from disordered structures, and naturally incorporates the chemical potential. This hybrid approach of lattice modeling and DFT may be useful to other self-organization processes where fluctuations are bound by discrete length scales in the system.

CHAPTER 4

Quantum Stability and Superconductivity of Immiscible Metal Ultrathin Alloy Films

Pb and Ga are immiscible in bulk form. Here, we show that atomically-smooth $\text{Pb}_{1-x}\text{Ga}_x$ ($x = 0.06$) alloy films can be stabilized on a $\text{Si}(111)-7 \times 7$ substrate through quantum confinement. Similar to the case of pure Pb, the alloy films initially follow a bilayer-by-bilayer growth mode but the resulting quantum growth morphology is remarkably different. The superconducting transition temperatures of the metastable alloy films indicate hole doping, supporting the notion that Ga atoms are substitutionally incorporated. The alloying experiments rule out previous explanations for the T_c suppression in Pb-based ultrathin films and furthermore indicate that critical supercurrents are already established in two-monolayer thin films.

4.1. Introduction

Self-assembled nanostructures have attracted much interest in the bottom-up approach to nanoscience and technology. Ultrathin metal films represent an interesting case in point in which the growth or assembly of the film is driven, under certain conditions, by electronic quantum confinement [Smith, 1996; Zhang, 1998; Tringides, 2000; Hong, 2003, Özer, 2005]. The relevant length scales in this process are the atomic layer spacing, the film thickness, and the Fermi wavelength. Because the Fermi wavelength is related to the carrier density, chemical doping or alloying should provide a means for controlling self-assembly of metallic nanostructures [Özer, 2007].

Doping is also a well-known paradigm for creating bulk electronic materials with desired chemical and electronic properties. A key challenge in controlled doping experiments is to minimize the potentially detrimental effects induced by chemical disorder and to avoid nucleation of unwanted thermodynamically favored precipitates. Low dimensional systems such as nanostructures, surfaces and thin materials offer the interesting opportunity for stabilizing doped systems with chemical compositions that are thermodynamically unfavorable and hence may display chemical or physical properties beyond what can be achieved via bulk synthesis. A particularly notable example is the stabilization of a surface alloy containing elements that are immiscible in the bulk for applications in heterogeneous catalysis [Besenbacher, 1998].

In this Chapter we show that immiscible elements such as Ga and Pb can form a metastable alloy in the ultrathin film regime where quantum size effects control the growth morphology. The resulting $\text{Pb}_{1-x}\text{Ga}_x$ ($x = 0.06$) alloy films are atomically smooth, crystalline, and superconducting. The critical temperature data obtained from these metastable alloy films offer a general insight into the origin of the T_c suppression in ultrathin films. Their magnetic hardness indicates the formation of a robust Bean-like critical state with exceptionally large critical current densities, exceeding those of pure Pb by a factor 2 ~ 3. Macroscopic phase coherence already appears to be established at 2 monolayers (ML).

4.2. Experimental Procedures

Pb and Ga were co-deposited in ultrahigh vacuum on an atomically clean Si(111)- 7×7 surface at 120 K. The deposition rate of Pb was calibrated by monitoring the Pb $4f_{7/2}$ core level intensity as a function of deposition time with X-ray photoelectron spectroscopy (XPS) (see Chapter 2). Briefly, the uptake of the XPS Pb intensity at 250 °C is linear with deposition time up to 1.3 ML (1 ML is 7.83×10^{14} atom/cm²). The Ga deposition rate was determined by monitoring the uptake of the Ga $2p_{3/2}$ core level intensity, using the Ga/Si(112) interface as our calibration standard. The absolute coverages of the Pb/Si(111) and Ga/Si(112) interfaces are known with great accuracy [Snijders, 2007; Feng, 2004].

As-deposited Pb_{1-x}Ga_x alloy films are quite rough, in contrast to as-deposited Pb films (not shown). They were post-annealed at 230 K to 300 K, depending on the thickness, so as to produce atomically smooth films (Figure 4.1). The morphology of the films was monitored with scanning tunneling microscopy (STM).

4.3. Results and Discussion

The minimum thickness for achieving smooth layer growth is 6 ML (not shown). At higher coverage, atomically smooth films are formed with 6 and 8 ML deep holes, as shown in Figures 4.1(a) and (b), respectively. The exposed layer thickness inside the holes can be estimated from the average hole size, considering mass conservation, and amounts to 2 ± 0.3 ML. The rather large error margin is due to the error in the XPS coverage calibration (Chapter 2). Independent deposition rate calibrations by STM only are within this margin of error. This growth morphology indicates a strong preference for bi-layer growth, which has been attributed to quantum size effects [Özer, 2005]. Interestingly, the depth and average diameter of the holes (~ 150 nm) is significantly larger than in pure Pb films.

The theoretical stability of thin films can be determined from its thickness dependent surface energy [Özer, 2005]. Figure 4.1(c) presents the results of first-principles density functional theory (DFT) calculations for the thickness dependent film energy using the Vienna *ab-initio* simulation package (VASP). The calculations were performed by Prof. Yu Jia at Zhengzhou University in China. The Perdew-Wang version of the generalized gradient approximation (GGA) was

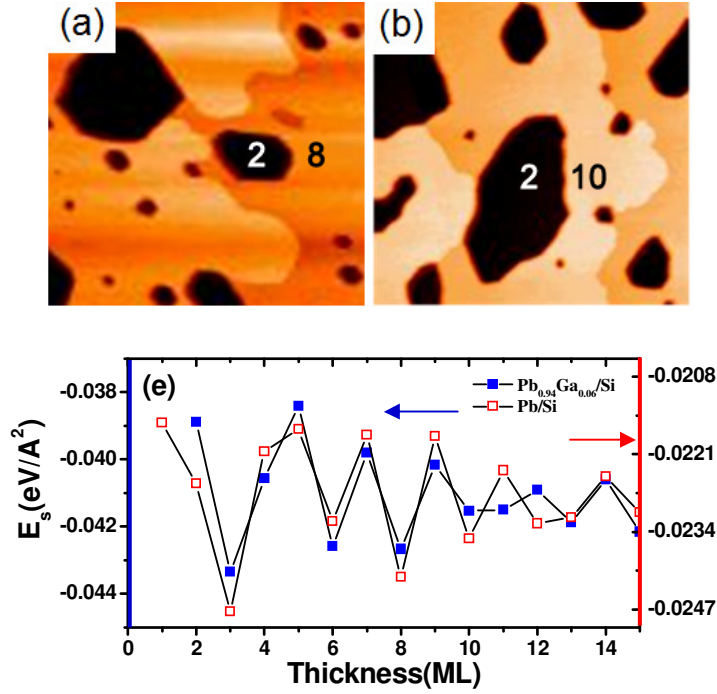


Figure 4.1

STM images of (a) a 6.9 ± 0.2 ML deposit showing only 6 ML deep holes ($500 \times 500 \text{ nm}^2$), and (b) a 8.5 ± 0.2 ML deposit showing only 8 ML deep holes ($500 \times 500 \text{ nm}^2$). Layer thicknesses are indicated in each panel and are measured from the Si(111) surface. (c) Thickness dependent surface energy of $\text{Pb}_{1-x}\text{Ga}_x$ for $x = 0.06$ films (filled squares) and of pure Pb films (open squares) from DFT.

performed with default plane-wave cutoffs of 144 eV. The $\text{Pb}_{0.94}\text{Ga}_{0.06}/\text{Si}(111)$ system was modeled by a 4×4 Pb supercell in which one Pb atom is replaced by a Ga atom. The calculations indicated stable layer thicknesses of $d = 6, 8$, and 10 ML, as shown in Figure 4.1(c), which is consistent with the experimental observation. The stable layer thicknesses are identical to those of pure Pb except for the precise location of even-odd crossover in the thin film stability of $\text{Pb}_{0.94}\text{Ga}_{0.06}$ near 11 ML. The calculations do not reproduce the preferred thickness of 2 ML.

To examine possible segregation of Ga atoms, we combined our STM measurements with XPS measurements as a function of temperature for a given film thickness. Figure 4.2(a) shows the intensity ratio of the Pb $4f_{7/2}$ and Ga $2p_{3/2}$ core levels of a co-deposited thin film with a

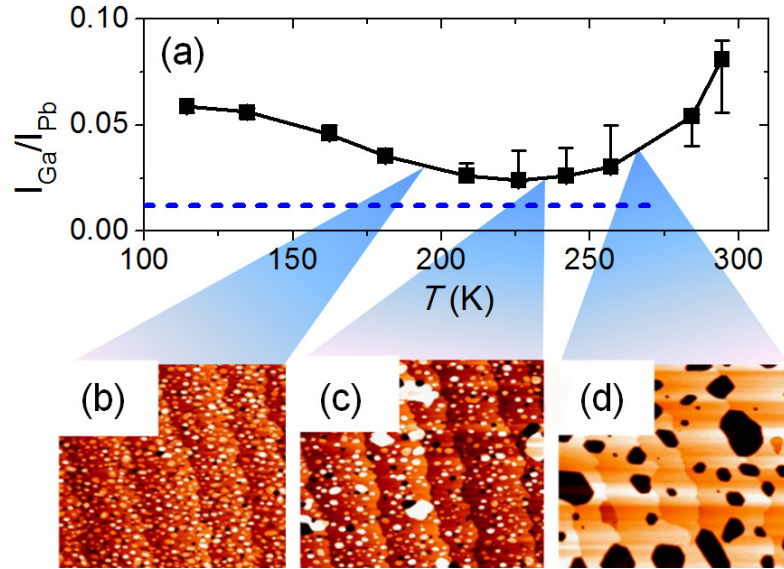


Figure 4.2

(a) Ratio of the Ga and Pb core level intensity as a function of temperature for a 8.5 ± 0.2 ML deposit. The dashed horizontal line corresponds to the measured intensity ratio when Ga (~ 0.5 ML) is deposited prior to Pb (~ 8.0 ML). Error bars reflect the spread of values over five experimental runs. (b-d) STM images ($700 \times 700 \text{ nm}^2$) obtained at three particular temperatures indicated in (a).

nominal coverage of 8.45 ML. The intensity ratio I_{Ga}/I_{Pb} of the as-deposited films is about 0.06. Because atom diffusion is very limited at 120 K, we tentatively consider this number representative of a homogeneous Ga distribution. This empirical ratio also shows good agreement with the estimated ratio of 0.07 from a layer-by-layer attenuation modeling for the XPS intensities for a 6 % $\text{Pb}_{1-x}\text{Ga}_x$ alloy, using mean free path values from the universal relation $\lambda_m = 538E^2 + 0.41(aE)^{1/2}$ [Seah, 1979].

For comparison, the XPS intensity ratio was also measured for sequential deposition experiments so as to mimic complete phase separation. First, we deposited 0.5 ML of Ga before adding the remaining 7.95 ML of Pb (i.e., the integrated amount of Ga and Pb being identical to that of the thin film alloy). In the second case, we deposited 7.95 ML of Pb, prior to depositing 0.5 ML of Ga. The XPS intensity ratios amounted to 0.01 and 0.20, respectively. On the other

hand, for the co-deposited thin film the XPS ratio is in between these two extreme values ranging from 0.03 to 0.07, depending on annealing temperature, indicating that some significant amount of Ga must be dissolved in the film.

The as-deposited film undergoes a morphological transition as temperature increases. This is shown in Figures 4.2(b)-(d), along with the measured XPS intensity ratio. While the initial decrease of the XPS intensity ratio seems to suggest that Ga atoms diffuse inward, it also coincides with the morphological transition of the film. When the XPS ratio reaches its minimum, one sees the first indications of quantum growth, as flat topped islands and 8 ML deep voids start to develop. The quantum morphology is complete around 270 K as shown in panel (d). Note that the I_{Ga}/I_{Pb} intensity ratio near 270 K is again similar to that of the as-deposited film (120 K). At still higher temperature, the surface becomes richer in Ga and above 300 K, the metastable alloy film breaks up into the Stranski-Krastanov (SK) morphology. While XPS experiments indicate that Ga is partially or completely dissolved up to 300 K, the distribution of dopants is difficult to establish.

The superconductive properties of the film corroborate the notion that Ga is incorporated as a dopant. The critical temperatures T_c of the $Pb_{1-x}Ga_x$ thin film superconductors were obtained from the onsets of the real part of the ac susceptibility in SQUID magnetometry experiments. For these ex-situ investigations, we sealed the meta-stable two-dimensional morphology of the alloy films with a 10 nm thick capping layer of amorphous Ge, deposited at 120 K in ultrahigh vacuum (UHV). The two-dimensional morphological stability of the capped layers at room temperature was verified with STM. However, we could not verify a possible redistribution of Ga under the capping layer. However, the superconductivity data indicate that Ga is dissolved in the Pb film. Figure 4.3(a) shows the measured T_c values as a function of the inverse film thickness, producing a linear plot. This indicates that

$$T_c(d) = T_{c0}(1 - d_c/d), \quad (4.1)$$

where T_{c0} is the (hypothetical) bulk T_c , and d_c is the critical thickness for the onset of thin film superconductivity. For comparison, we included the $T_c(d)$ values of atomically smooth Pb films and $Pb_{1-x}Bi_x$ ($x = 0.11$ and 0.2) alloy films from earlier studies [Özer, 2006a; Özer, 2006b; Özer, 2007]. Extrapolation of $T_c(d)$ versus $1/d$ with $d \rightarrow \infty$ produces T_{c0} values of 7.2 K, 7.7 K and 8.05 K for bulk Pb and bulk $Pb_{1-x}Bi_x$ ($x = 0.11$ and 0.2) alloys, respectively. Here, the extrapolated T_c of a hypothetical $Pb_{1-x}Ga_x$ ($x = 0.06$) bulk alloy is around 6.95 K, slightly suppressed compared to

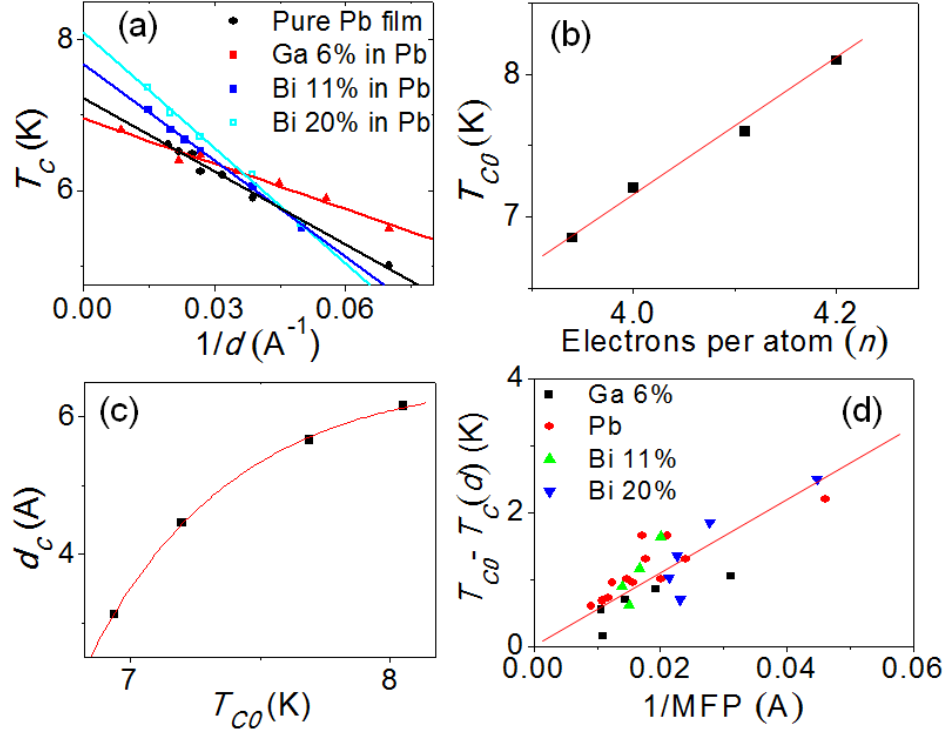


Figure 4.3

(a) Critical temperature as a function of inverse film thickness: $\text{Pb}_{1-x}\text{Bi}_x$ ($x = 0.11$ (filled squares) and 0.2 (open squares)), pure Pb (circles), and $\text{Pb}_{1-x}\text{Ga}_x$ ($x = 0.06$) (triangles) obtained from the onset of the real part of the ac magnetization (data of pure Pb and PbBi alloy films were taken from ref. [Özer, 2007]). (b) Extrapolated bulk T_{c0} versus the average number of electrons per atom. (c) Critical thickness for the onset of superconductivity, d_c , versus the bulk $T_c(d)$. The offset $T_{c0} - T_c(d)$ as a function of the inverse mean free path ($1/l$).

pure Pb. The latter is to be expected for Group III dopants [Dynes, 1975]. Figure 4.3(b) shows that the extrapolated bulk T_c is clearly correlated with the electron concentration n in the alloy material. The linear variation between T_{c0} and n was also noted in studies on bulk alloys and has been interpreted in terms of the changing electron-phonon coupling throughout the alloy series [Dynes, 1975].

The thin film alloy experiments shed new light on the mechanism of the T_c suppression in ultrathin films. The latter is usually interpreted in terms of a boundary value problem for the superconducting order parameter [Simonin, 1986], or in terms of a suppression of the electron-phonon coupling parameter λ [Shanenko, 2009; Brun, 2009]. Both scenarios would suggest that

d_c decreases for increasing values of the bulk λ_b . For instance, in Refs. [Shanenko, 2009; Brun 2009] it was suggested that the electron-phonon coupling constant in thin films has the following form:

$$\lambda(d) = \lambda_b (1 - \lambda^*/d) \quad (4.2)$$

where λ^* is a positive constant. Substituting Eq. (4.2) into the BCS gap equation

$$k_B T_C(d) = \hbar \omega_D(d) \exp(-1/\lambda(d)) \quad (4.3)$$

and using Eq. (4.1), one can easily show that

$$d_c \approx \lambda^*/\lambda_b = \lambda^* \ln \hbar \omega_D - \lambda^* \ln k_B T_{c0} \quad (4.4)$$

where $\omega_D(d) \approx \omega_D$ is the Debye frequency of the film. This indicates that the critical thickness d_c should *decrease* as the bulk T_{c0} increases (due to *e.g.* Bi alloying). However, Figure 4.3(c) shows that d_c increases as T_{c0} increases. This indicates that either the electron-phonon coupling is enhanced in the thin film limit, or that the T_c suppression in thin films may be due to some other mechanism, such as scattering. For instance, it is known that impurities suppress T_c provided that the gap parameter is weakly anisotropic. In the case of non-magnetic scattering, $T_c(d) = T_{c0} - \frac{\pi \hbar}{8\tau} (1 - \langle \Omega \rangle^2)$, where $\tau = l/v_f$ is the scattering time for nonmagnetic impurities (l is the mean free path and v_f is the Fermi velocity) and $\Omega(k)$ is the angular part of the gap function [Kogan, 2002]. If $\langle \Omega \rangle^2 \ll 1$ (weak anisotropy), then $T_{c0} - T_c(d) \sim l^{-1}$. As shown in Figure 4.3(d), $T_c(d) - T_{c0}$, is indeed proportional to the inverse mean free path of the Ga, Pb, and Bi alloy systems. Here the mean free path values were obtained from analysis of upper critical field measurement (not shown) [Özer, 2005]. The relatively slow suppression of $T_c(d)$ in the Pb-Ga alloy films indicates that scattering should also be relatively weak (compared to the Pb-Bi thin film alloys).

Figure 4.4(a) shows the dc magnetization loops at different temperatures for a 10 ML film with 8-ML-deep holes. The magnetization is almost perfectly irreversible (*i.e.*, the loops are rectangular) up to quite high temperatures (5.25 K). Evidently, the film behaves as an ideal Bean-type superconductor indicating macroscopic phase coherence. This is attributed to strong vortex pinning by the 8 ML deep holes. Strikingly, the dc magnetic moment (and critical current density $J_c \propto m$) increases as the temperature increases up to 3.25 K. This anomaly is also observed in the real part of the ac magnetization (not shown). The imaginary part of m ($m = m' + im''$) of the ac

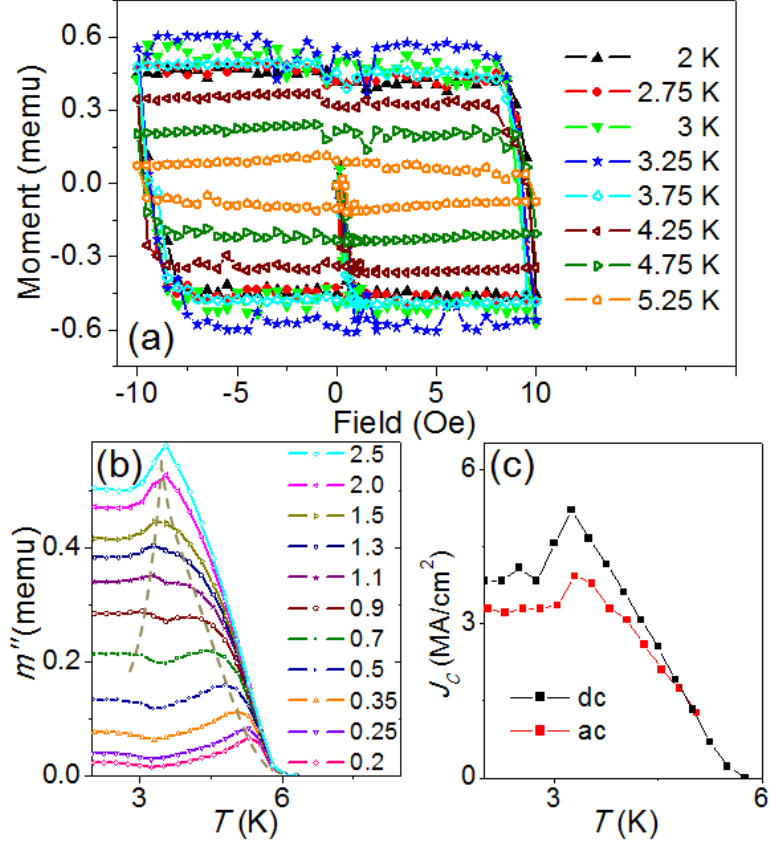


Figure 4.4

(a) Magnetization loops at different temperature for a 10 ML alloy film with 8 ML-deep voids. (b) Imaginary part of the ac magnetic response measured with the ac field amplitudes shown. (c) Critical current densities obtained from the dc magnetization loops at 5 Oe in (a) and by fitting χ'' versus $2h_{ac}/J_c d$ to the critical state model, according to Clem and Sanchez [Clem, 1994] (see Figure 4.5).

magnetic response is shown in Figure 4.4(b) and reveals two peaks below 1.3 Oe ac field as indicated by the dashed lines, which merge at about 3.25 K. For the ac response, J_c values were determined by scaling the h_{ac} values with a factor $2/J_c d$ so as to fit the χ'' vs h_{ac} values of the Bean model (see Figure 4.5), following refs. [Clem, 1994; Özer, 2006a]. The $J_c(T)$ values obtained from the dc and ac magnetic measurements are shown in Figure 4.4(c). Both indicate the existence of a maximum $J_c(T)$ at 3.25 K, amounting to about 5.5 MA/cm² for the 10 ML alloy film.

The exceptional occurrence of a maximum in J_c (Figure 4.4(c)) cannot be explained from a

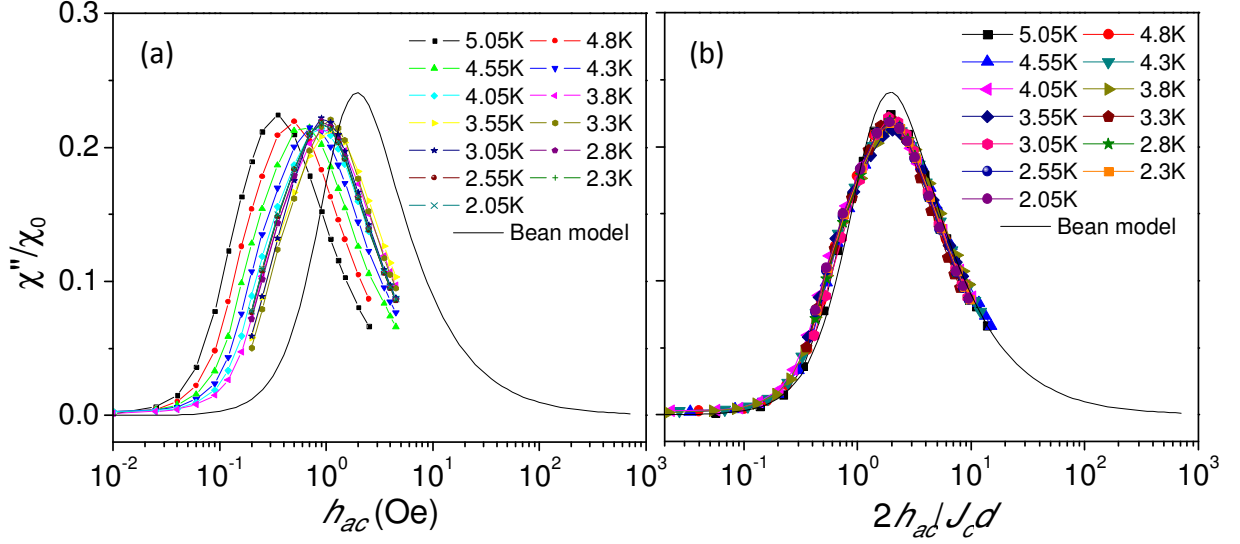


Figure 4.5

(a) Normalized χ'' vs ac amplitude at different temperatures of a 10 ML Pb-Ga alloy film and an ideal Bean-type superconductor in disk-shape. (b) Fitting χ'' versus $2h_{ac}/J_c d$ to the critical state model, according to Clem and Sanchez [Clem, 1994].

conventional vortex pinning scenario and should most likely be attributed to the highly unusual quantum growth morphology of these metastable alloys. In Ref. [Özer, 2007], it was shown that in atomically smooth films containing blind holes, $J_c \sim J_d(\Delta d/d)$ where Δd is the hole depth and J_d the depairing current density. If the first two monolayers exposed by the voids in the Pb-Ga film are in the superconducting state, the depth of the pinning center equals 8 ML. However, if the first two monolayers exposed by the voids in the Pb-Ga film are in the normal state, the depth of the pinning center equals the total film thickness (10 ML). We conjecture that below 3.25 K, the first two monolayers inside the voids become superconducting so that the depth of the pinning center is reduced from 10 ML above 3.25 K to 8 ML below 3.25 K. Accordingly, J_c should be reduced by a factor of 8/10 upon lowering the temperature through 3.25 K, which is close to the observed reduction in Figure 4.4(c). Note that such a phenomenon would be difficult to observe in pure Pb films because Δd is only 2ML and the T_c values of the neighboring film thicknesses d and $(d - \Delta d)$ are almost identical. In this context, we note that superconductivity has recently been established in 2 ML Pb films below 4 K via scanning tunneling spectroscopy (STS), which is a local probe [Qin, 2009]. The present results strongly suggest that it is even possible to establish

macroscopic phase coherence in a 2 ML thin film below 3.25 K, perhaps with some assistance from proximity coupling to the thick film regions.

4.4. Summary

Atomically smooth alloy films of thermodynamically immiscible metal elements have been stabilized through the quantum size effect (QSE). Incorporation of Ga atoms is indicated by XPS and superconducting property measurements. Alloying experiments offer a new perspective for identifying the nature of the T_c suppression in ultrathin films. Critical supercurrents are already established at 2 ML.

CHAPTER 5

Influence of Interface Reconstruction on the Formation and Superconductive Properties of metastable Pb-Ga Alloy Films

The growth, composition, and superconductive properties of $\text{Pb}_{1-x}\text{Ga}_x$ alloy films ($x \leq 0.06$) strongly depend on the atomic structure of the interface. Whereas alloy films on $\text{Si}(111)-7 \times 7$ grow in bilayers, reminiscent of the quantum growth phenomenon of pure Pb layers, alloy films grown on the $\text{Si}(111)-\sqrt{3} \times \sqrt{3}-\text{R}30^\circ\text{-Ga}$ and $\text{Si}(111)-\sqrt{3} \times \sqrt{3}-\text{R}30^\circ\text{-Pb}$ interfaces exhibit classical layer-by-layer growth. The (7×7) interface is unique in that it enables formation of atomically smooth alloy films containing up to 6% of Ga, which is far beyond the solid solubility limit. In contrast, the $\sqrt{3}$ interfaces promote phase separation. The contrasting influences of these interfaces are also reflected by their superconducting properties, most notably by the more than one order of magnitude difference in the critical current density. The results underscore the unique role of the quantum growth morphology in establishing robust critical currents at the nanoscale and furthermore show how template modification or “interface engineering” might be used to alter self-organization and collective properties in the nanophase.

5.1. Introduction

The substrate plays a critical role in thin film heteroepitaxy. Thin film growth is determined by a variety of thermodynamic and kinetic growth parameters, many of which can be related to – and in some cases controlled by – the atomic-scale structure and mesoscopic morphology of the starting substrate. By choosing a proper substrate, the structure, morphology and properties of a thin film material can often be engineered to desirable qualities but, arguably, the most interesting cases are those in which deposited atoms self-organize into a novel nanophase material. Interesting examples include the formation of optically active quantum dots and quantum-dot superlattices in Si/Ge [Liu, 2000] and PbSe/PbTe heteroepitaxy [Springholz, 1998; Springholz, 2000], metallic nanowires in silicide heteroepitaxy, or the formation of atomically smooth metals films on semiconductor surfaces. While the formation of wires and dots appears to be driven by a classical strain relaxation mechanism, the formation of atomically smooth metal films is driven by quantum-mechanical confinement. The substrate is essential in both cases because it determines the strain energy and quantum mechanical boundary condition.

Atomically clean substrates are often reconstructed. The surface reconstruction can be altered or eliminated by deposition of (sub)-monolayer (ML) amounts of a third species, prior to thin film deposition. Such template modification can facilitate smooth layer growth through surfactant [Vrijmoeth, 1994; Hornvohoege, 1994] or interfactant action [Jałochowski, 1988; Schmidt, 2001] or it can be used to control the band offset or Schottky barrier at the hetero-structure interface [Tung, 1984; Heslinga, 1990]. In this Chapter, we show how modification of a Si(111)- 7×7 template into a Si(111)- $\sqrt{3} \times \sqrt{3}$ -R30° template prior to the deposition of a thin $\text{Pb}_{1-x}\text{Ga}_x$ alloy film ($x \leq 0.06$) reduces the kinetic solubility of the Ga, switches the growth mode of the alloy film from the quantum-mechanical to classical regime, and produces a dramatic contrast in the critical state properties of these thin film superconductors. The results underscore the unique role of the quantum growth morphology in establishing robust critical currents at the nanoscale and furthermore show how template modification or “interface engineering” might be used to alter self-organization and collective properties in the nanophase.

5.2. Experimental Procedures

$\text{Pb}_{1-x}\text{Ga}_x$ alloy films ($x \leq 0.06$) were grown by co-deposition of Ga and Pb onto the clean Si(111)- 7×7 surface, the Si(111)- $\sqrt{3} \times \sqrt{3}$ -R30°-Ga and the Si(111)- $\sqrt{3} \times \sqrt{3}$ -R30°-Pb interface (henceforth $\sqrt{3}$ -Ga and $\sqrt{3}$ -Pb interfaces, respectively) at 120 K in ultrahigh vacuum, using effusion cells. The nominal thickness of the films is close to eight atomic layers or 8 ML. (For thickness-dependent studies of $\text{Pb}_{1-x}\text{Ga}_x$ alloy films on Si(111)- 7×7 , we refer the reader to Chapter 4). In order to achieve atomically smooth film morphologies, the as-deposited films were annealed to ~ 250 K.

The deposition rate of Pb was calibrated by monitoring the Pb $4f_{7/2}$ core level intensity in x-ray photoelectron spectroscopy (XPS) as a function of deposition time while maintaining the Si(111)- 7×7 substrate at 250 °C. At this temperature, the core level intensity increases linearly with deposition time up to the saturation coverage. The Ga deposition rate was determined in a similar fashion by monitoring the growth of the Ga $2p_{1/2}$ core level intensity as a function of deposition time on a Si(112) reference substrate. The absolute saturation coverages of Pb on Si(111)- 7×7 at 250 °C and Ga on Si(112) at 535 °C are known with accuracy better than ten percent (see Chapter 4).

The $\sqrt{3}$ -Pb interface was prepared by depositing 1/3 ML of Pb on top of clean Si(111)- 7×7 at 250 °C, following the procedures by Ganz et al [Ganz, 1991]. The $\sqrt{3}$ -Ga phase was prepared by depositing approximately, 1.5 ML of Ga onto a clean Si(111)- 7×7 surface at room temperature. The substrate was subsequently heated at 650°C to evaporate the excess Ga for about 5 minutes while monitoring the $(\sqrt{3} \times \sqrt{3})$ spot intensity with LEED. The annealing was stopped when the $(\sqrt{3} \times \sqrt{3})$ LEED pattern was fully developed. The existence of the $\sqrt{3}$ phases was verified with scanning tunneling microscopy (STM).

The superconductive properties of the films were explored ex-situ by SQUID magnetometry, following the procedures of Özer et al. [Özer, 2006a]. Briefly, the samples were sealed with an amorphous Ge capping layer deposited at 120 K, prior to removal from vacuum. STM experiments verified that the atomically smooth morphology of the metal films remains preserved under the capping layer, at least up to room temperature. The capped samples were subsequently inserted into the SQUID magnetometer and stored in a desiccator.

5.3. Results and Discussion

Figures 5.1(a) and (b) show the STM images of a 7-ML-thick $\text{Pb}_{1-x}\text{Ga}_x$ alloy film ($x \leq 0.06$) showing 1-ML islands deposited onto the $\sqrt{3}\text{-Pb}$ and $\sqrt{3}\text{-Ga}$ interfaces, respectively. The nominal coverage is 7.5 ML. The alloy films grow according to the *classical* layer-by-layer growth mode and remain atomically smooth up to room temperature, showing monatomic step heights at non-integer coverages. In contrast, $\text{Pb}_{1-x}\text{Ga}_x$ alloy films on the $\text{Si}(111)\text{-}7 \times 7$ surface grow in bilayers, which is characteristic of strong *quantum size effects* on the growth mode (Chapter 4). The alloy films on $\text{Si}(111)\text{-}7 \times 7$ are furthermore uniquely characterized by the presence of large 8-ML deep holes, as shown in Figure 5.1(c). The lateral dimensions of the holes can easily reach

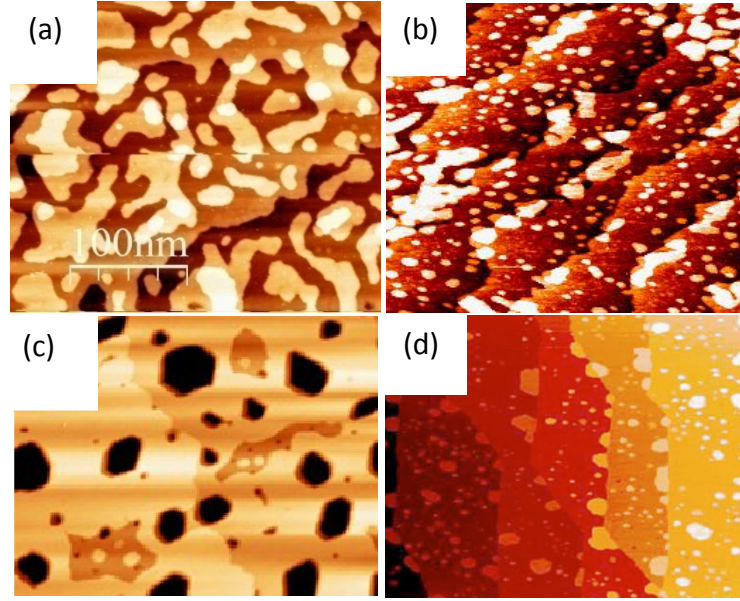


Figure 5.1

STM images of a 7.5-ML-deposited $\text{Pb}_{1-x}\text{Ga}_x$ alloy film on the $\sqrt{3}\text{-Pb}$ interface (a) and $\sqrt{3}\text{-Ga}$ interface (b), showing atomically smooth mesas bounded by 1 ML-high steps. The image sizes are $(300 \times 300) \text{ nm}^2$ and $(500 \times 500) \text{ nm}^2$, respectively. (c) STM image of a 7.5 ML $\text{Pb}_{1-x}\text{Ga}_x$ alloy film on $\text{Si}(111)\text{-}7 \times 7$ showing an atomically smooth film with large 8-ML deep holes. The image size is $(700 \times 700) \text{ nm}^2$. (d) STM image of an 8 ML deposited pure Pb film showing 2 ML-tall mesas. The image size is $(700 \times 700) \text{ nm}^2$ (Image from [Özer, 2006b]).

Table 5.1

Observed growth modes of Pb and $\text{Pb}_{1-x}\text{Ga}_x$ alloys on the $\text{Si}(111)7\times 7$, $\sqrt{3}\text{-Pb}$ and $\sqrt{3}\text{-Ga}$ interfaces.

Interfaces Films	(7×7)	$(\sqrt{3} \times \sqrt{3})\text{-Pb}(\alpha)$	$(\sqrt{3} \times \sqrt{3})\text{-Ga}(\alpha)$
Pure Pb film (~ 8 ML deposited)	Bi-layer growth	Bi-layer growth	$\times$
Pb-Ga alloy film (7.5 ML deposited)	Bi-layer growth	Single layer growth	Single layer growth

several hundred Ångstrom. Finally, pure Pb films are known to grow in bilayers on both the (7×7) and $\sqrt{3}\text{-Pb}$ interfaces. For instance, Figure 5.1(d) shows the morphology of an 8 ML deposited pure Pb film on $\text{Si}(111)\text{-}7 \times 7$ [Özer, 2006a]. The bilayer growth mode is evident from the 2 ML tall mesas that decorate the surface (and from the absence of monolayer steps). Pure Pb films do not exhibit the 8 ML deep holes seen in the alloy films on $\text{Si}(111)\text{-}7 \times 7$. Another noticeable difference between the $\sqrt{3}$ and (7×7) interfaces is that the two dimensional morphology on the $\sqrt{3}$ interfaces appears to be stable up to at least 300 K whereas the pure Pb and $\text{Pb}_{1-x}\text{Ga}_x$ alloys films on $\text{Si}(111)\text{-}7 \times 7$ ball up above 250 K. These observations are summarized in Table 5.1.

Ga and Pb are immiscible in the bulk. However, in Chapter 4 we concluded that atomically smooth $\text{Pb}_{1-x}\text{Ga}_x$ alloy films can be stabilized on $\text{Si}(111)\text{-}7 \times 7$ up to $x \leq 0.06$. Here, we investigate how the solubility of Ga in Pb is qualitatively affected by the nature of the substrate interface. To this end, we measured the intensity ratio of the Ga $2p_{1/2}$ and Pb $4f_{7/2}$ core levels in XPS. For $\text{Pb}_{1-x}\text{Ga}_x$ alloy films grown on $\text{Si}(111)\text{-}7 \times 7$, the ratio $I_{\text{Ga}}/I_{\text{Pb}} \approx 0.07$ after annealing and smoothening of the film at 250 K. This ratio is consistent with a nominal Ga percentage of about 6% (see Chapter 4). On the other hand, for the alloy films formed on the $\sqrt{3}\text{-Ga}$ and $\sqrt{3}\text{-Pb}$ interfaces, $I_{\text{Ga}}/I_{\text{Pb}} \approx 0.01$ indicating that nearly all Ga atoms diffused toward the buried interface. The “alloy” films on the $\sqrt{3}$ interfaces are thus depleted of Ga and their composition must be close to that of pure Pb; nonetheless they do not exhibit the bilayer growth morphology seen in the pure Pb films on $\text{Si}(111)\text{-}7 \times 7$ and $\sqrt{3}\text{-Pb}$.

The superconductive properties of the 7.5 ML deposited alloy films on the (7×7) and $\sqrt{3}$ interfaces were investigated ex-situ by SQUID magnetometry. Figure 5.2 shows the dc magnetic moments m of the $\text{Pb}_{1-x}\text{Ga}_x$ films grown on $\text{Si}(111)-7 \times 7$ (squares), $\sqrt{3}$ -Pb (triangles pointing up) and $\sqrt{3}$ -Ga (triangles pointing down) as a function of the applied magnetic field, recorded at 2 K. (The moments are produced by the superconductive currents that screen the applied dc magnetic field). For comparison, we also included the dc magnetic moment loops of slightly underdosed (diamonds) and slightly overdosed (circles) pure Pb films with a nominal coverage close to 8 ML [Özer, 2006a]. The contrasting magnetic properties of the pure Pb films exhibiting 2 ML deep blind holes (underdosed) or 2 ML tall mesas (overdosed), specifically the high critical current density ($J_c \propto m$) and magnetic hardness of the Pb films with holes, were attributed to strong vortex pinning by the 2-ML deep blind holes [Özer, 2006b].

The magnetic volumes of all samples are approximately equal and, consequently, the different moments in Figure 5.2 reflect the differences in the critical current densities that these

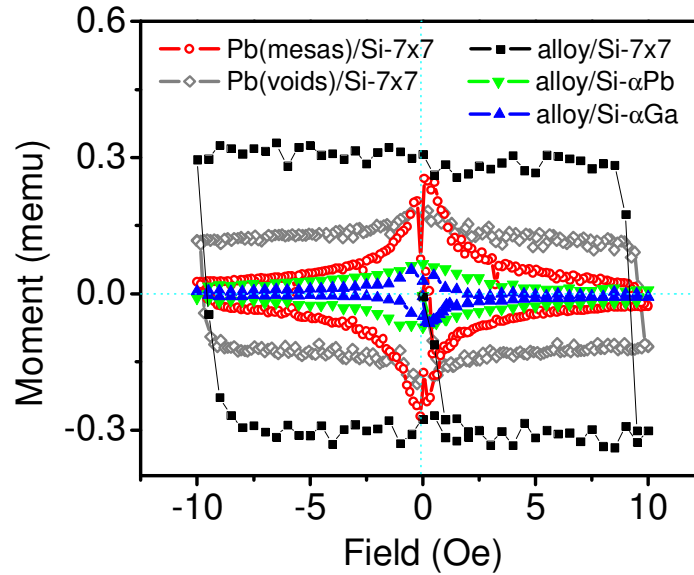


Figure 5.2

dc Magnetization loops at 2 K of 7.6 ML thick $\text{Pb}_{1-x}\text{Ga}_x$ ($x \leq 0.06$) alloy films, grown on $\text{Si}(111)-7 \times 7$ ($\blacksquare$), $\sqrt{3}$ -Pb ($\blacktriangledown$) and $\sqrt{3}$ -Ga ($\blacktriangle$). Previously published data for pure Pb films on $\text{Si}(111)-7 \times 7$ exhibiting 2-ML tall mesas ($\circ$) or 2-ML deep voids ($\diamond$) are shown for comparison [Özer, 2006b].

films can support as a function of the magnetic field. The dc magnetizations of the $\text{Pb}_{1-x}\text{Ga}_x$ and underdosed Pb films on $\text{Si}(111)\text{-}7 \times 7$ are almost perfectly irreversible (*i.e.*, the loops are rectangular). Evidently, both films behave as ideal Bean-type superconductors, implying strong vortex pinning, but the critical current density of the alloy film is a factor ~ 2.5 higher than that of pure Pb. The latter is consistent with the fact that the pinning centers (*i.e.*, holes) of the alloys films on (7×7) are 8 ML deep, compared to the 2 ML depth of the pinning centers in pure Pb.

The critical current density can be obtained from the magnetic moment via the critical-current relation $J_c = 30\Delta m/Vr$ where m is the measured magnetic moment, V the volume of the film, and r is the macroscopic radius of the sample (≈ 1.5 mm). J_c amounts to 1.3 MA/cm^2 (for 2 ML voids) and 3.0 MA/cm^2 for Pb and $\text{Pb}_{1-x}\text{Ga}_x$, respectively, at 2 K and 5 Oe dc field. In contrast to the hard magnetization loops for the (7×7) interfaces, magnetization loops of alloy films grown on the $\sqrt{3}$ interfaces indicate that J_c strongly decreases as a function of the magnetic field, which precludes accurate determination of J_c at 5 Oe dc field.

To acquire the full temperature dependence of the critical current density, we measured the ac magnetic response ($m = m' + im''$) as a function of the ac driving amplitude (Figure 5.3). J_c can be determined from the peak position of the imaginary magnetic response using $J_c = 1.03h_{ac}/d$ at the peak position where h_{ac} is the amplitude of the ac modulation field and d is film

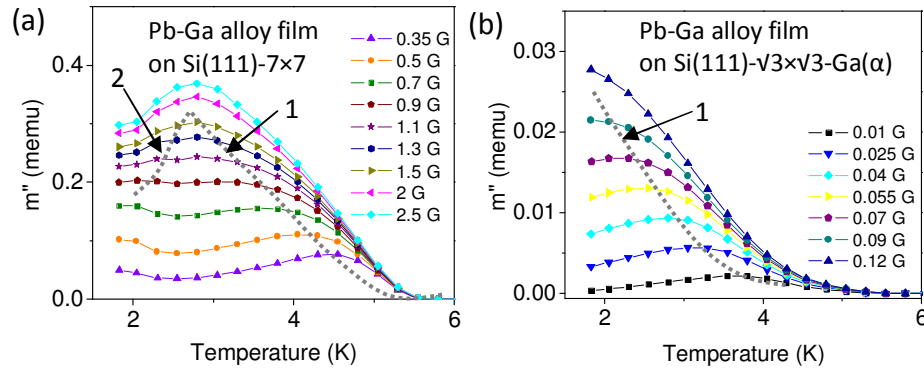


Figure 5.3

Imaginary part m'' of the ac magnetic response of a 8-ML-thick $\text{Pb}_{1-x}\text{Ga}_x$ alloy film grown on (a) $\text{Si}(111)\text{-}7 \times 7$, and (b) the $\sqrt{3}\text{-Ga}$ interface, measured in 5 G dc field. Dotted gray lines trace the locations of the peaks in m'' .

thickness. The critical current densities from the ac and dc measurements are generally in good agreement, indicating strong macroscopic phase coherence.

Figures 5.3(a) and (b) show the imaginary part of m of the ac magnetization of a 7.5 ML $\text{Pb}_{1-x}\text{Ga}_x$ alloy film on the (7×7) and $\sqrt{3}$ -Ga interfaces, respectively. Notice the qualitative and quantitative differences for the materials grown on the two interfaces. Using the m'' values, we find that for 2 K and 5 Oe dc field, $J_c \sim 0.1 \text{ MA/cm}^2$, 0.3 MA/cm^2 , and 3.0 MA/cm^2 for alloy films grown on the $\sqrt{3}$ -Ga, $\sqrt{3}$ -Pb, and (7×7) interfaces, respectively. This remarkable difference in critical current density of more than one order of magnitude highlights the contrasting pinning-potential landscape for the (7×7) and $\sqrt{3}$ interfaces.

The imaginary response in Figure 5.3(a) is not only an order of magnitude larger but also shows a double peak structure at small driving amplitudes, as indicated by the dotted gray lines. In Chapter 4, we attributed the double peak feature to the existence of the 8-ML deep holes and a vortex depinning phenomenon near 3 K as the bottom of the holes become superconducting. In contrast, m'' for the $\sqrt{3}$ -Ga interface only reveals one peak shifting monotonically toward lower temperature as the driving amplitude increases, as shown in Figure 5.3(b). According to the relation $J_c = 1.03h_{ac}/d$, this monotonic shift implies a monotonic increase of J_c as the temperature is lowered. This ac response is similar to that of pure Pb films (not shown here). Alloys grown on Si(111)- 7×7 thus appear to have unique pinning properties which, again, is related to the unique presence of 8-ML deep holes in these films.

The upper critical field or $H_{c2}(T)$ of the films was determined from the onset of the real part of the ac magnetization as a function of the applied dc field perpendicular to the film. Figure 5.4 shows some representative $H_{c2}(T)$ data of the alloy films. Pure Pb data are included for comparison. At low temperature, the upper critical field of the alloy films decreases linearly with temperature, as given by the Ginzburg-Landau (GL) theory. However, in the vicinity of T_c , the $H_{c2}(T)$ data deviate significantly from the linear GL behavior, showing opposite curvature for the (7×7) and $\sqrt{3}$ interfaces. The origins of these contrasting curvatures are not well understood. The T_c values vary from 5.6 K for pure Pb, to 5.8 K and 6.0 K for the alloys on the $\sqrt{3}$ -Ga and (7×7) interface. Note that T_c for the $\sqrt{3}$ -Ga interface assumes an intermediate value suggesting that the Ga content of the film is reduced compared to the (7×7) case.

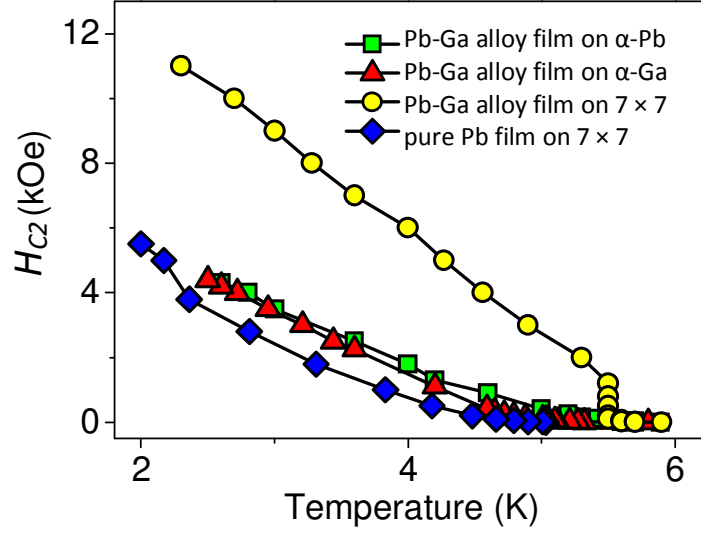


Figure 5.4

$H_{c2}(T)$ values of pure Pb and $\text{Pb}_{1-x}\text{Ga}_x$ alloy films for the various interface reconstructions. The nominal coverages are 7.5 ML for Pb-Ga alloy films and ~ 8 ML for pure Pb films. $H_{c2}(T)$ was obtained from the onset of diamagnetic screening as a function of temperature, in various dc fields. The data were measured using a 10 mG probing amplitude.

The upper critical field is related to carrier scattering via the Ginzburg-Landau expression $H_{c2}(T) = \Phi_0 / 2\pi\xi_{\text{GL}}^2(T)$ and the interpolation formula

$$\xi_{\text{GL}}(T, d) \cong 0.739 \left\{ \xi_0^{-2} + 0.882 [\xi_0 \times l(d)]^{-1} \right\}^{-1/2} \times (1 - T/T_c)^{-1/2} \quad (5.1)$$

where $\xi_{\text{GL}}(T)$ is the GL coherence length of the films, Φ_0 the magnetic flux quantum, and $\xi_0(d) = \xi_0^{\text{bulk}} \times T_{c0} / T_c(d)$ is the normalized BCS coherence length. From the upper critical field at 2 K, we obtain the scattering mean free paths of the $\text{Pb}_{1-x}\text{Ga}_x$ alloys on $\sqrt{3}$ -Ga and (7×7) . They were determined to be 70 Å and 32 Å, respectively, which amounts to $3.5\times$ and $1.1\times$ the film thickness. The reduced scattering for the $\sqrt{3}$ -Ga interface is consistent with the notion that the alloy films on the $\sqrt{3}$ -Ga interface are depleted of Ga and, consequently, there are fewer impurity scatterers. Qualitatively, however, the large deep holes can be expected to contribute to scattering of carriers, perhaps significantly so. The fact that the $H_{c2}(T)$ values of the alloy films on

the $\sqrt{3}$ interfaces is similar to those of pure Pb on Si(111)- 7×7 (Figure 5.4) suggests that interface scattering contributes little to the contrasting superconductive properties of the (7×7) and $\sqrt{3}$ interfaces.

5.4. Summary

In summary, we have shown that the growth, composition, and superconductive properties of $\text{Pb}_{1-x}\text{Ga}_x$ alloy films are strongly affected by the atomic scale nature of the starting interface. The alloy films on Si(111)- 7×7 grow in bilayers, reminiscent of the quantum growth of pure Pb layers, but in addition they exhibit large 8-ML deep holes. In contrast, alloy films on the $\sqrt{3}$ -Ga and $\sqrt{3}$ -Pb interfaces exhibit a classical layer-by-layer growth mode, resulting in films that are completely closed. The alloy composition of the films is also strongly affected by the nature of the interface. Specifically, the 7×7 interface stabilizes alloy compositions well beyond the solid solubility limit. In contrast, alloy films on the $\sqrt{3}$ interfaces phase separate with most of the Ga accumulating at the interface. The contrasting properties of these interfaces are also reflected by their superconducting properties, most notably by the more than one order of magnitude difference in the critical current density. The results not only underscore the unique role of the quantum growth morphology in establishing robust critical currents at the nanoscale but also show how template modification or “interface engineering” might be used to alter self-organization and collective properties in the nanophase.

CHAPTER 6

Quantum size effects on the excitation and damping of volume plasmons in ultrathin film

Low temperature growth of Mg on Si(111) results in the formation of atomically smooth thin films with precisely controlled thickness. We monitored the evolution of plasmon loss satellites in the Mg 1s core level photoemission spectrum as a function of the film thickness. The loss energy of the bulk plasmon is inversely proportional to the square of the film thickness, indicating the existence of quantized bulk plasmons. The loss spectrum is dominated by the $n=3$ antisymmetric normal mode, consistent with the theoretical prediction (hydrodynamics and random phase approximation) that symmetric plasmons have vanishing spectral weight in the ultrathin limit. The overall suppression of the plasmon loss intensity in the ultrathin limit is attributed to Landau damping. These observations are striking manifestations of the role of size quantization on plasmon resonances in precisely controlled nanostructures.

6.1. Introduction

Plasmons are collective excitations of the electron gas inside a metal, which usually resonate at optical or ultraviolet frequencies [Atwater, 2007]. The coupling between bulk plasmons and an external electromagnetic field creates a hybrid excitation known as the plasmon polariton. In addition, surfaces and interfaces can accommodate two-dimensional plasmons, and the corresponding surface plasmon polaritons are recognized as the key enablers for confining electromagnetic waves to sub-wavelength features such as ultra-small waveguides, thin films, or other metallic nano-objects. This “squeezing of light” into volumes smaller than the classical diffraction limit offers great opportunities for innovative discoveries in a diverse set of scientific and technological disciplines, ranging from optics [Vučković, 2000], information technology, sensors, catalysis, and basic energy sciences [McFarland, 2003; Mapel, 2007; Regan, 1991].

Nearly all the efforts in the area of “nano-plasmonics” involves optimization of the spatial confinement—and to some limited extent, the resonant frequency— of the surface plasmon polariton in artificially structured arrays of metallic nanostructures, such as nanogrooves or nanodots. The underlying physics is still adequately captured by classical electrodynamics (generalized Mie theory). On the other hand, nano-objects are inherently quantum mechanical (i.e., discrete) in nature, suggesting the intriguing possibility of tuning the resonant frequency and decay of quantum confined plasmon modes as a function of the object’s dimensions and boundary conditions. As will be shown in this Chapter, this can be accomplished in ultrathin film materials with atomically precise thicknesses and quantized electronic structures.

Strictly speaking, ultrathin films cannot support bulk or surface plasmons. When the film thickness d is large enough to support its own charge density profile, a *multipole* surface plasmon mode develops at the vacuum-overlayer interface [Tsuei, 1991; Liebsch, 1991]. Its resonance peaks at about $0.8\omega_p$ where ω_p is the bulk plasmon energy of the film material. The more familiar *monopole* surface plasmon mode develops when the $qd > 1.5$ where q is the wave vector of the collective excitation. It is important to note that these surface excitations resonate below the bulk plasmon frequency.

It is much less clear, however, how the bulk collective excitations or multipole ‘volume plasmons’ develop as a function of the film thickness. The existence of plasmon standing waves in ultrathin films was indicated by faint anomalies in the optical properties, suggesting some

resonant enhancement phenomenon at the standing wave frequencies [Lindau, 1970; Anderegg, 1971; Abelès, 1980]. The interpretation of optical transmission spectra, specifically the identification of collective modes, surface effects, film quality and thickness calibration have all been questioned in subsequent experimental [Abelès, 1980; Yuh, 1996] and theoretical works [Feibelman, 1975; Heinonen, 1993; Schaich, 1994]. However, the basic premise regarding the existence of longitudinal plasmon waves seems to be correct.

Bulk plasmons are difficult to detect in low energy electron loss spectroscopy (EELS) experiments. EELS is surface sensitive and the impinging electron's charge will be screened by the surface plasmons. In this Chapter, we employ XPS to directly probe the plasmons that are generated inside atomically-smooth, ultrathin Mg(0001) films whose thickness is known with monolayer accuracy. The surface and volume plasmons are excited via the sudden creation of a core hole in photoemission and by inelastic scattering of the outgoing photoelectrons, processes that are commonly referred to as "intrinsic" and "extrinsic" plasmon excitations, respectively [Pardee, 1975; Norman, 1979; Biswas, 2003]. The excitations show up as distinctive loss features or shake-up satellites in XPS spectra. In simple metals such as bulk Mg and Al, intrinsic processes account for approximately 25% of the plasmon loss intensity [Biswas, 2003]. For films with thicknesses between 6 and 25 atomic layers the energy losses are inversely proportional to the square of the film thickness. These results are consistent with the existence of quantized plasmons, which we interpret on the basis of theoretical (hydrodynamics and random-phase approximation) descriptions of the density-response function [Eguiluz, 1979]. The core level spectra also reveal how size quantization increases the Landau damping and photoelectron mean free path, shuts off collective screening, amplifies the role of low-energy electron-hole excitations, and enhances Auger decay of the core hole. Quantum confined thin films thus also provide a novel platform for studying the interplay between the various many-body aspects of core level photoemission as a function of a single control parameter d .

6.2. Experimental Procedures

Experiments were carried out in an ultra-high vacuum system equipped with XPS, a variable temperature STM, and several effusion cells. High purity Mg was evaporated onto a Si(111)- 7×7 surface kept at 120 K. Low temperatures are necessary to avoid silicide formation and to

promote the growth of atomically smooth films. The Mg deposition rate was calibrated with STM by following the evolution of the thin film morphology and energy location of the quantum well states as a function of film thickness [Abelle, 2002]. This yielded a tentative result of (0.12 ± 0.02) ML/min, which will be refined below.

6.3. Results and Discussion

Figure 6.1 shows the Mg $1s$ core level spectra of 2 – 25 ML thick Mg films emission, recorded at an angle of $\theta = 22^\circ$ measured from the normal direction. The most intense feature around 183 eV kinetic energy (KE) corresponds to the zero-loss spectrum of the Mg $1s$ core level. The first loss peak appears at ~ 7.2 eV lower KE and corresponds to surface plasmon. The loss feature at ~ 11 eV lower KE is identified as the volume (bulk) plasmon satellite. Higher order loss features are seen at even lower KE.

The exact peak positions and line shapes were determined via a least squares fitting

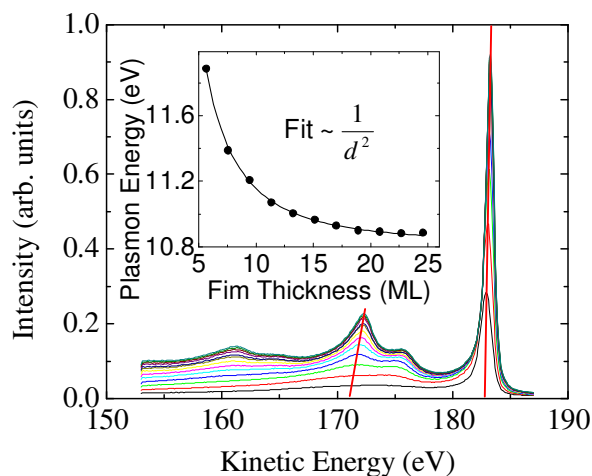


Figure 6.1

Photoelectron intensity as a function of kinetic energy of the Mg $1s$ core level for film thicknesses in the range 2-25 ML. Surface and bulk plasmon losses as well as higher order loss satellites are seen on the low kinetic energy side of the spectra. Red lines roughly indicate the positions of the no-loss and bulk plasmon peaks. Their kinetic energy difference corresponds to the plasmon loss energy, which is plotted as a function of film thickness in the inset.

procedure after subtracting the background using the Shirley algorithm [Shirley, 1972]. The background subtracted spectra were fitted with Gaussian convoluted Doniach-Šunjić lineshapes [Doniach, 1969]. The Inset of Figure 6.1 shows the resulting volume plasmon energy as a function of $1/d^2$ for film thicknesses ranging from 6 to 25 ML. The data fall onto a perfectly straight line which extrapolates to a bulk plasmon frequency of 10.83 eV, in excellent agreement with bulk studies [Chen, 1976]. The $1/d^2$ scaling can be readily explained noticing that the vertical wave vector is quantized according to $q_z = n\pi/d$ (where n is a quantum number) and samples the bulk dispersion which is quadratic in q . Note, however, that only one particular quantum number would reproduce the correct bulk dispersion. In order to determine the quantum number, we generated several sets of q_z values for each value of n ranging from 1 to 5 using the experimentally determined film thickness d . To calculate the film thickness, we slightly adjusted our preliminary result for the evaporation rate to 0.126 ML/min. so that our energy loss data fall exactly on top of the bulk dispersion (solid line in Figure 6.2). This agreement works perfectly well only if the quantum number $n=3$. The other quantum numbers (dotted lines) require

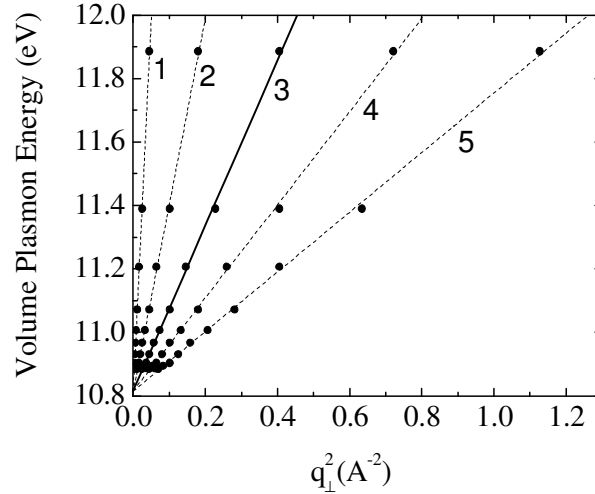


Figure 6.2

Bulk plasmon energies plotted as a function of q_z^2 . Each dotted line is labeled by the quantum number n which is used to calculate the corresponding q_z values. Only the solid line reproduces the bulk dispersion relation (see text).

assumptions about the film thickness that are outside our confidence interval from the initial thickness determination. Note, however, that the $n = 1, 2, 4, 5$ excitations might be buried in the tails of the loss spectrum since the width of the plasmon satellite exceeds the spacing between the discrete plasmon levels especially at higher thicknesses. For example, the energy difference between the $n = 1$ and $n = 5$ modes in 6, 7, and 25 ML films amounts to 2.83, 1.59, and 0.15 eV, respectively, whereas the width of the satellite is of the order of 2 – 3 eV.

A simple qualitative picture explaining why the energy loss spectrum peaks for $n = 3$ can be gleaned from the imaginary part of the density-response function for the hydrodynamic model of a confined electron gas with symmetric boundaries (thus ignoring the role of the substrate). Via a simple Fourier transform, the imaginary part of the dynamical density-response function $\chi(\vec{q}_{||}, \omega | zz')$ yields the dynamical structure factor, which is directly measured by the scattering of fast (photo-) electrons. In the limit of large wave lengths, the poles of the density-response function correspond to sinusoidal density fluctuations that are either symmetric (S) or anti-symmetric (A) under reflection about the mid plane of the film, respectively, which is true in both hydrodynamics and random phase approximations (RPA). Numerical analysis of the spectral weights associated with these modes—in particular, their dependence with film thickness—indicated that the A-modes strongly dominate, the leading excitation corresponding to the $n = 3$ density fluctuation (the $n = 1$ mode has negligible weight because it only exists below very small values of $q_{||}$) [Eguiluz, 1979; Mukhopadhyay, 1980]. Note that, strictly speaking, this argument only applies to extrinsic plasmon losses.

The satellite intensities reveal how the collective density fluctuations decay in the ultrahigh quantum limit [Norman, 1979]. Figure 6.3(a) shows the absolute intensity of the Mg 1s core level as a function of the film thickness. The intensity ratio of the first volume plasmon satellite $I(1, d)$ and the main line $I(0, d)$ is shown in Figure 6.3(b). The relative plasmon intensity saturates much slower than the main peak. Its uptake is determined by the plasmon creation cross section, or equivalently by a corresponding mean free path (*mfp*). The faster saturation of the no-loss peak must be attributed to additional (i.e., single-particle) loss mechanisms. It can be fitted using $I(0, d) = I(0, \infty) [1 - e^{-d/\lambda \cos(\theta)}]$ where $I(0, d)$ is the intensity of the zero-loss line for thickness d , and λ is the total *mfp*.

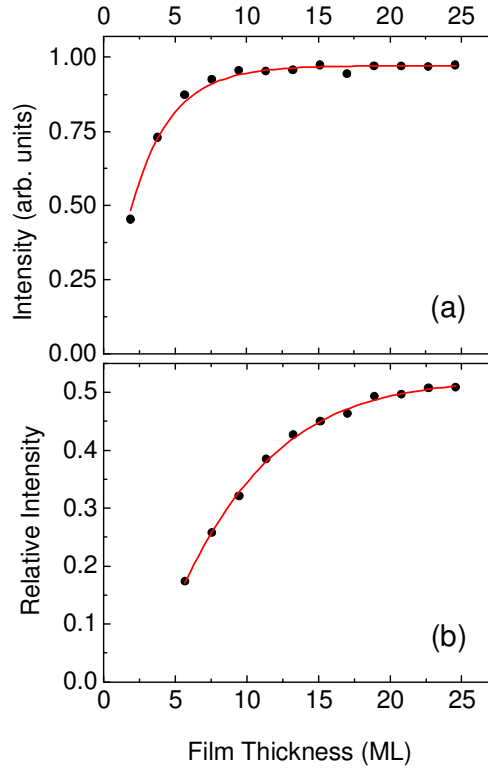


Figure 6.3

Intensity of the main peak (a) and bulk plasmon satellite (b) as a function of film thickness. The satellite intensity is normalized to the intensity of the main peak. Solid curves show best fits to the data.

Following Mahan's random spatial emission model [Norman, 1979; Mahan, 1973; Gervasoni, 1992; Šunjić, 1974; Inglesfield, 1983], the intensity of the n th bulk plasmon satellite in photoemission can be written as a discrete summation over atomic layers as follows:

$$I(n, d) = \sum_{m=0}^{N-1} \frac{(\beta + md_0/l)^n}{n!} \exp[-(\beta + md_0/l)] \exp(-md_0/L). \quad (6.1)$$

Here β is the intrinsic plasmon coupling parameter, l the mfp due to extrinsic plasmon collisions, L the mfp for other loss processes (excluding plasmon creation), $Nd_0 = d$, and $d_0 = 2.61 \text{ \AA}$

(interplanar spacing). After performing the summation, the data in Figure 6.3(b) are fitted using the resulting formula

$$I(1, d) / I(0, d) = \beta + \frac{d}{l} x \frac{N x^{N-1} (x-1) - x^N + 1}{(x-1)(x^N - 1)} \quad (6.2)$$

where $x \equiv \exp[-d(l+L)/lL]$. This procedure yields an unphysical negative value for β [Mahan, 2000; Biswas, 2003]. Attempts to cure this problem using a different (linear) background subtraction and different fitting constraints were unsuccessful. A simple remedy is to assume that the plasmon creation probability decreases in the thin film limit. Specifically, a positive requires that $l(d)$ increases as the film thickness decreases. Simple trial functions such as $l(d) \propto 1/d^2$ produced satisfactory fits to both relative plasmon intensity and no loss intensity (improving the latter one also). While those fits cannot be taken too seriously, Figure 6.3(b) indicates that the plasmon loss channel is gradually shut off for diminishing film thickness which is indicative of stronger Landau damping.

To assess the role of Landau damping in the ultrathin film limit, we define the origin of coordinates to lie in the mid-plane of the film, by setting $z = (d/2) + u = L + u$, where $2L = d$, and $-L \leq u \leq +L$ and recast Eq. (2.24) from Ref [Eguiluz, 1979] in the following form:

$$\begin{aligned} \text{Im } \chi(\vec{q}_{\parallel}, \omega | uu') &= \left(\frac{1}{d^2} \right) \sum_{l, l' = \pm 1, \pm 2, \dots} \cos k_l u \cos k_{l'} u' \text{Im } \chi(\vec{q}_{\parallel}, \omega | k_l k_{l'}) \\ &+ \left(\frac{1}{d^2} \right) \sum_{l, l' = 0, \pm 1, \pm 2, \dots} \sin k_l u \sin k_{l'} u' \text{Im } \chi(\vec{q}_{\parallel}, \omega | k_l k_{l'}) , \end{aligned} \quad (6.3)$$

where in the first term (the “even” part of the response), $k_l = 2l\pi/d = l\pi/L$, and in the second term (the “odd” part of the response) $k_l = (2l+1)\pi/d = (l+1/2)\pi/L$. The Fourier components are given by [Eguiluz, 1979]

$$\begin{aligned} \chi(\vec{q}_{\parallel}, \omega | kk') &= \left(\frac{d}{2} \right) \chi_B(\vec{q}, \omega) (\delta_{k, k'} + \delta_{k, -k'}) \\ &- \frac{2q_{\parallel}}{4\pi e^2} \frac{v(\vec{q}) \chi_B(\vec{q}, \omega) v(\vec{q}') \chi_B(\vec{q}', \omega)}{D^{(S, A)}(\vec{q}, \omega)} \end{aligned} \quad (6.4)$$

where $\chi_B(\vec{q}, \omega) = \chi_0(\vec{q}, \omega) / (1 - v(\vec{q}) \chi_0(\vec{q}, \omega))$ is the RPA density-response function in the bulk, and $\chi_0(\vec{q}, \omega)$ the well-known Lindhard function [Mahan, 2000]. The denominators $D^{(S,A)}(\vec{q}, \omega)$ in Eq. (6.4) are defined by

$$D^{(S,A)}(\vec{q}, \omega) = 1 + \frac{1}{d} \sum_{\substack{k \\ (even \\ odd)}} \frac{2q_{\parallel}}{q_{\parallel}^2 + k^2} \frac{1}{\epsilon_B^{RPA}(\vec{q}_{\parallel}, k; \omega)} \quad (6.5)$$

Inserting Eq. (6.4) and (6.5) into Eq. (6.3) gives the following RPA result for the dynamical response function of an ultrathin metal slab:

$$\begin{aligned} \text{Im } \chi^{RPA}(\vec{q}_{\parallel}, \omega | uu') &= \left(\frac{1}{2d} \right) \sum_l \cos k_l u \cos k_l u' \text{Im } \chi_B^{RPA}(\vec{q}_{\parallel}, k_l; \omega) \\ &+ \left(\frac{1}{2d} \right) \sum_l \sin k_l u \sin k_l u' \text{Im } \chi_B^{RPA}(\vec{q}_{\parallel}, k_l; \omega) , \end{aligned} \quad (6.6)$$

For small wave vectors $\text{Im } \chi_B^{RPA}(\vec{q}_{\parallel}, k_l; \omega)$ will be dominated by the plasmon pole. Eq. (6.6) will be dominated by the excitation channel corresponding to the odd term for $l = 1$, *i.e.*,

$$\text{Im } \chi^{RPA}(\vec{q}_{\parallel}, \omega | uu') = \left(\frac{1}{2d} \right) \sin k_{l=1} u \sin k_{l=1} u' \text{Im } \chi_B^{RPA}(\vec{q}_{\parallel}, k_{l=1}; \omega) . \quad (6.7)$$

where $k_{l=1} = (3/2)\pi/L$. The geometrical $1/d$ factor seems to suggest that plasmon losses are enhanced in the ultrathin film limit. However, the crucial point is that according to Eq. (6.7), the dynamical response in ultrathin films mirrors the dynamical response in the bulk: $\chi_B(\vec{q}, \omega)$. As the film (half-) thickness L decreases, the magnitude of the 3D wave vector $\vec{q} = (\vec{q}_{\parallel}, k_{l=1} \sim 1/L)$ grows. Eventually, even for modest values of $q_{\parallel}$, $|\vec{q}|$ will reach the critical value q_c (typically q_c^{-1}), for which the plasmon will decay into electron-hole pairs [Zacharias, 1975]. This condition signals the situation in which the plasmon scattering of the emerging XPS electron is shut-off, leading to an enhanced mean-free path.

Figure 6.4 shows the binding energy, hole lifetime, and Doniach-Šunjić asymmetry parameter [Doniach, 1969] α of the Mg 1s core level as a function of the film thickness. The

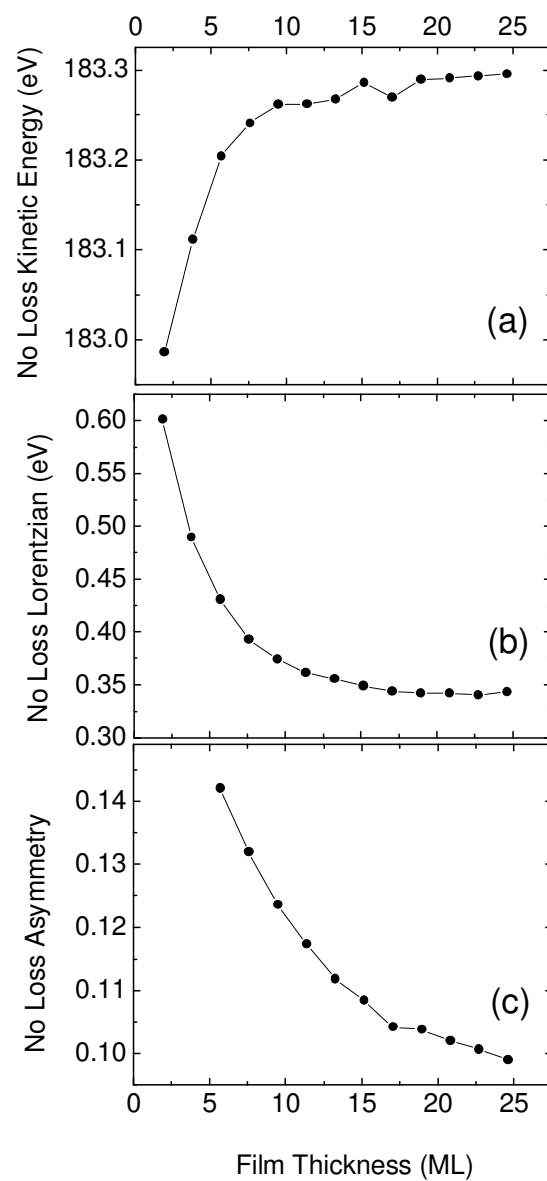


Figure 6.4

Kinetic Energy (a), Lifetime broadening (b), and Asymmetry parameter (c) of the no loss peak obtained from fittings to Doniach-Šunjić lineshapes.

damping of the plasmon satellite intensity is accompanied by a small screening shift to higher binding energy and an increased spectral weight from low-energy electron-hole excitations. Because the intrinsic part of the core level spectrum $A(\omega)$ obeys the spectral sum rule $\int \omega A(\omega) d\omega = E_0$ where E_0 represents the Hartree-Fock energy of the frozen 1s orbital [Egelhoff, 1987], the suppression of high-energy satellites naturally leads to the binding energy shift and increased asymmetry of the main line [Despoja, 2008]. The decreased hole lifetime in the thin film limit is also consistent with this interpretation. The response time of plasmons to a sudden perturbation is of the order of the inverse plasmon energy, meaning that the core excitations are already screened by the rapid plasmon response before the contracted valence levels of the core-ionized atom acquire significant population density via charge transfer from the surrounding medium [Gunnarsson, 1978]. The population of these valence levels dictates the subsequent Auger decay and, consequently, the lifetime of the core hole. Because the short-time response is dominated by plasmon excitation, strong Landau damping in the ultrathin limit is consistent with the observed lifetime shortening. Ultrathin films thus provide a compelling platform for studying plasmon oscillations, Landau damping, and the collective screening response of a low-dimensional electron system as a function of quantum mechanical confinement.

6.4. Summary

We succeeded in growing atomically smooth Mg films on Si(111) with precisely controlled film thickness. We monitored the evolution of the plasmon loss satellites in the Mg 1s XPS core level spectrum. For films with thicknesses between five and twenty five atomic layers the plasmon energy is inversely proportional to the square of the film thickness, consistent with the existence of quantized plasmons, which we interpret on the basis of theoretical (hydrodynamics and random-phase approximation) descriptions of the density-response function. We demonstrate that the plasmon loss feature is dominated by the $n = 3$ *antisymmetric* normal mode of the thin film. While the normal-mode excitations are classical in nature, the plasmon decay mechanism is controlled by quantum mechanics.

References

- [Abelès, 1980] F. Abelès, Y. Borensztein, M. De Crescenzi, and T. Lopez-Rios, *Surf. Sci.* **101**, 123 (1980)
- [Abelle, 2002] L. Abelle, C. Rogero, and K. Horn, *Phys. Rev. B* **65**, 125319 (2002)
- [Anderegg, 1971] M. Anderegg, B. Feuerbacher, and B. Fitton, *Phys. Rev. Lett.* **27**, 1565 (1971)
- [Ashby, 1947] W.R. Ashby, *J. Gener. Psych.* **37**, 125 (1947)
- [Atwater, 2007] H. Atwater, “The Promise of Plasmonics”, Scientific American, 2007.
- [Bak, 1987] P. Bak, *Rep. Prog. Phys.* **45**, 587 (1987)
- [Ball, 1994] P. Ball, “*Designing the Molecular World*”; Princeton University Press: Princeton, (1994)
- [Bardeen, 1961] J. Bardeen, *Phys. Rev. Lett.* **6**, 57 (1961)
- [Bartelt, 1992] N. C. Bartelt, T. L. Einstein and E. D. Williams, *Surf. Sci.* **276**, 308 (1992)
- [Beck, 2004] M. Beck, A. van de Walle and M. Asta, *Phys. Rev. B* **70**, 205337 (2004)
- [Besenbacher, 1998] F. Besenbacher, I. Chorkendorff, B. S. Clausen, B. Hammer, A. M. Molenbroek, J. K. Nørskov and I. Stensgaard, *Science* **279**, 1913 (1998)
- [Biswas, 2003] C. Biswas, A. K. Shukla, S. Banik, V. K. Ahire, and S. R. Barman, *Phys. Rev. B* **67**, 165416 (2003)
- [Brun, 2009] C. Brun, I-Po Hong, F. Patthey, I. Yu. Sklyadneva, R. Heid, P. M. Echenique, K. P. Bohnen, E. V. Chulkov and Wolf-Dieter Schneider, *Phys. Rev. Lett.* **102**, 207002 (2009)
- [Brune, 1998] H. Brune and M. Giovannini and K. Bromann and K. Kern, *Nature* **394**, 451 (1998)
- [Butz, 1992] R. Butz and S. Kampers, *Phys. Rev. Lett.* **61**, 1307 (1992)
- [Čechal, 2007] J. Čechal, et al., *J. Phys.: Condens. Matter* **19**, 016011 (2007)
- [Chambers, 1986] S.A. Chambers, F. Xu, H.W. Chen, I.M. Vitomirov, S.B. Anderson, and J.H. Weaver, *Phys. Rev. B* **34**, 6605 (1986)
- [Chan, 2003] T-L. Chan, C. Z. Wang, M. Hupalo, M. C. Tringides, Z-Y. Lu, and K. M. Ho, *Phys. Rev. B* **68**, 045410 (2003)
- [Chen, 1994] X. Chen, F. Wu, Z. Zhang and M. G. Lagally, *Phys. Rev. Lett.* **73**, 850 (1994)
- [Chen, 1976] C. H. Chen, *J. Phys. C: Solid State Phys* **9**, L321 (1976)
- [Ciobanu, 2004] C. V. Ciobanu, D. T. Tambe and V. B. Shenoy, *Surf. Sci.* **556**, 1 (2004)
- [Clem, 1994] J.R. Clem and A. Sanchez, *Phys. Rev. B* **50**, 9355 (1994)
- [Crain, 2006] J. N. Crain, M. D. Stiles, J. A. Stroscio, and D. T. Pierce, *Phys. Rev. Lett.* **96**, 156801 (2006)
- [Crottini, 1997] A. Crottini, D. Cvetko, L. Floreano, R. Gotter, A. Morgante, and F. Tommasini, *Phys. Rev. Lett.* **79**, 1527 (1997)
- [Demkov, 1995] A.A. Demkov, J. Ortega, O.F. Sankey and M.P. Grumbach, *Phys. Rev. B* **52**, 1618 (1995)
- [Doniach, 1969] S. Doniach and M. Šunjić, *J. Phys. C* **3**, 285 (1969).
- [Dynes, 1975] R.C. Dynes, and J.M. Rowell, *Phys. Rev. B* **11**, 1884 (1975)
- [Egelhoff, 1987] W.F. Egelhoff, *Surf. Sci. Rep.* **6**, 253 (1987)
- [Eguiluz, 1979] A.G. Eguiluz, *Phys. Rev. B* **19**, 1689 (1979)
- [Feibelman, 1975] P. J. Feibelman, *Phys. Rev. B* **12**, 4282 (1975)
- [Feibelman, 1983] P. J. Feibelman, *Phys. Rev. B* **27**, 1991 (1983)
- [Filipe, 1997] A. Filipe, A. Schuhl, and P. Galtier, *App. Phys. Lett.*, **70**, 129 (1997)
- [Feng, 2004] R. Feng, E.H. Conrad, M.C. Tringides, C. Kim, and P.F. Miceli, *Appl. Phys. Lett.* **85**, 3866 (2004)
- [Ganz, 1991] E. Ganz, I.-S. Hwang, F. Xiong, K. Silva Theiss, and J. Golovchenko, *Surf. Sci.* **257**, 259 (1991)
- [Gavioli, 1999] Luca Gavioli, Kevin R. Kimberlin, Michael C. Tringides, John F. Wendelken, and Zhenyu Zhang, *Phys. Rev. Lett.* **82**, 129 - 132 (1999)
- [Gervasoni, 1992] J.L. Gervasoni and N. R. Arista, *Surf Sci* **260**, 329 (1992)
- [González, 2004] C. González, P. C. Snijders, J. Ortega, R. Pérez, F. Flores, S. Rogge, and H. H. Weitering, *Phys. Rev. Lett.* **93**, 126106 (2004)
- [Gunnarsson, 1978] O. Gunnarsson, and K. Schönhammer, *Solid State Commun.* **26**, 147 (1978)
- [Heinonen, 1993] O. Heinonen and W. Kohn, *Phys. Rev. B* **48**, 12240 (1993)
- [Heslinga, 1990] D.R. Heslinga, H.H. Weitering, D.P. van der Werf, T.M. Klapwijk, and T. Hibma, *Phys. Rev. Lett.* **64**, 1589 (1990)
- [Hibino, 1996] H. Hibino, T. Ogino, *Phys. Rev. B* **54**, 5763 (1996)
- [Himpsel, 2001] F.J. Himpsel, A. Kirakosian, J. N. Crain, et al., *Solid State Commun.* **117**, 149 (2001)

- [Hinch, 1989] B. J. Hinch, C. Koziol, J. P. Toennies, and G. Zhang, *Europhys. Lett.* **10**, 341 (1989)
- [Hong, 2003] H. Hong, C.-M. Wei, M. Y. Chou, et al., *Phys. Rev. Lett.* **90**, 076104 (2003)
- [Hornvонhoegeen, 1994] M. Hornvонhoegeen, *App. Phys. A*, **59**, 503 (1994)
- [Hupalo, 2002] M. Hupalo and M. C. Tringides, *Phys. Rev. B* **65**, 115406 (2002)
- [Hupalo, 2003] M. Hupalo, J. Schmalian, and M. C. Tringides, *Phys. Rev. Lett.* **90**, 216106 (2003)
- [Inglesfield, 1983] J. E. Inglesfield, *J. Phys. C: Solid State Phys* **16**, 403 (1983)
- [Jalochowski, 1988] M. Jalochowski, E. Bauer, *J. Appl. Phys.* **63**, 4501 (1988)
- [Jia, 2006] Y. Jia, et al., *Phys. Rev. B* **74**, 035433 (2006)
- [Kogan, 2002] V. G. Kogan, *Phys. Rev. B* **66**, 020509 (2002)
- [Kohler, 1992] U. Kohler, O. Jusko, B. Muller, M. H. von Hoegen and M. Pook, *Ultramicroscopy*, **42**, 832 (1992)
- [Lang, 1971] N. D. Lang and W. Kohn, *Phys. Rev. B* **3**, 1215 (1971)
- [LeGoues, 1989] F. K. LeGoues, M. Copel, R. M. Tromp, *Phys. Rev. Lett.* **63**, 1826 (1989)
- [Li, 2000] A. Li, F. Liu, D. Y. Petrovykh, J.-L. Lin, et al., *Phys. Rev. Lett.* **85**, (2000)
- [Liebsch, 1991] A. Liebsch, *Phys. Rev. Lett.* **67**, 2858 (1991)
- [Lindau, 1970] I. Lindau and P. O. Nilsson, *Phys. Lett.* **31A**, 352 (1970)
- [Liu, 1997] F. Liu F, and M. G. Lagally, *Surf. Sci.* **386**, 169 (1997)
- [Liu, 2000] Liu J. L., Jin G., Tang Y. S., et al. *Appl. Phys. Lett.* **76**, 586 (2000)
- [Losio, 2000] R. Losio, K. N. Altmann, and F. J. Himpsel, *Phys. Rev. B* **61**, 10845 (2000)
- [Ma, 2007] X. C. Ma, P. Jiang, Y. Qi, J. F. Jia, Y. Yang, W. H. Duan, W. X. Li, X. Bao, S. B. Zhang, Q. K. Xue, *Proc. Nat. Acad. Sci.* **104**, 9204 (2007)
- [MacLeod, 2007] J. M. MacLeod, D. Psiachos, et al., *J. of Phys.: Conference Series* **61**, 800 (2007)
- [Mahan, 1973] G. D. Mahan, *Phys. Stat. Sol. B* **55**, 703 (1973)
- [Mahan, 2000] G. D. Mahan, Many-Particle Physics, 3rd Edition (Kluwer Academic, New York, 2000).
- [Mapel, 2007] J. K. Mapel, M. Singh, M. A. Baldo, K. Celebi, *Appl. Phys. Lett.* **90**, 121102 (2007),
- [Marchenko, 1980] V. I. Marchenko and A. Ya. Parshin, *Sov. Phys. JETP*. **52**, 129 (1980)
- [McFarland, 2003] E. W. McFarland, J. Tang, *Nature* **421** 616 (2003)
- [Mo, 1998] Y. W. Mo, J. Kleiner, M. B. Webb, and M. G. Lagally, *Phys. Rev. Lett.* **66**, 1998 (1991)
- [Mukhopadhyay, 1980] G. Mukhopadhyay and S. Lundqvist, *Solid State Commun.* **33**, 115 (1980)
- [Nurminen, 2003] L. Nurminen, F. Tavazza, D. P. Landau, A. Kuronen and K. Kaski, *Phys. Rev. B* **68**, 085326 (2003)
- [Norman, 1979] D. Norman, and D. P. Woodruff, *Surf. Sci.* **79**, 76 (1979)
- [Özer, 2005] M. M. Özer, et al., *Phys. Rev. B* **72**, 113409 (2005)
- [Özer, 2006a] M. M. Özer, et al., *Phys. Rev. B* **74**, 235427 (2006)
- [Özer, 2006b] M. M. Özer, et al., *Nature Physics* **2**, 173 (2006)
- [Özer, 2007] M. M. Özer, et al., *Science* **316**, 1594 (2007)
- [Pardee, 1975] W. J. Pardee et al., *Phys. Rev. B* **11**, 3614 (1975)
- [Pfennigstorf, 2002] O. Pfennigstorf, A. Petkova, H. L. Guenter, et al. *Phys. Rev. B* **65**, 045412 (2002)
- [Qin, 2009] S. Qin, J. Kim, Q. Niu and C.-K. Shih, *Science*, 324, 1324 (2009)
- [Reedijk, 2003] M. F. Reedijk, J. Arsic, D. Kaminski, P. Poodt, J. W. M. van Kessel, W. J. Szweryn, H. Knops, E. Vlieg, *Phys. Rev. Lett.* **90**, 056104 (2003)
- [Schaich, 1994] W. L. Schaich and J. F. Dobson, *Phys. Rev. B* **49**, 14700 (1994)
- [Schmidt, 2001] Th. Schmidt, E. Bauer, *Surf. Sci.* **480**, 137 (2001)
- [Schulte, 1976] F. K. Schulte, *Surf. Sci.* **55**, 427 (1976)
- [Seah, 1979] M. P. Seah and W. A. Dench, *Surf. and Interface Anal.* **1**, 2 (1979)
- [Shanenko, 2009] A. A. Shanenko, M. D. Croitoru and F. M. Peeters, *Phys. Rev. B* **75**, 014519 (2009)
- [Shirley, 1972] D. A. Shirley, *Phys. Rev. B* **5**, 4709 (1972).
- [Simonin, 1986] J. Simonin, *Phys. Rev. B* **33**, 7830 (1986)
- [Smith, 1996] A. R. Smith, K.-J. Chao, Q. Niu and C.-K. Shih, *Science* **273**, 226 (1996)
- [Snijders, 2005] P. C. Snijders, C. G. S. Rogge, C. González, J. Ortega, R. Pérez, F. Flores and H. H. Weitering, *Phys. Rev. B* **72**, 125343 (2005)
- [Snijders, 2006] P. C. Snijders, S. Rogge, and H. H. Weitering, *Phys. Rev. Lett.* **96**, 076801 (2006)

- [Snijders, 2007] P.C. Snijders, E. J. Moon, C. González, S. Rogge, J. Ortega, F. Flores and H. H. Weitering, *Phys. Rev. Lett.* **99**, 116102 (2007)
- [Springholz, 1998] G. Springholz, V. Holy, M. Pinczolis and G. Bauer, *Science* **282**, 734 (1998)
- [Springholz, 2000] G. Springholz, M. Pinczolis, P. Mayer, et al. *Phys. Rev. Lett.* **84**, 4669 (2007)
- [Stepanovsky, 2006] S. Stepanovsky, M. Yakes, V. Yeh, M. Hupalo, M.C. Tringides, *Surf. Sci.* **600** 1417 (2006)
- [Su, 2001] W.B. Su, S.H. Chang, W.B. Jian, C.S. Chang, L.J. Chen, and T.T. Tsong, *Phys. Rev. Lett.* **86**, 5116 (2001)
- [Šunjić, 1974] M. Šunjić and D. Šokčević, *J. Elec. Spec. Rel. Phen.* **5**, 963 (1974)
- [Takayanagi, 1985] K. Takayanagi, Y. Tanishiro, S. Takahashi, et al. *Surf. Sci.* **164**, 367 (1985)
- [Tersoff, 1992] J. Tersoff, *Phys. Rev. B* **45**, R8833 (1992)
- [Tsuei, 1991] K-D Tsuei, E. W. Plummer, and P. J. Feibelman, *Phys. Rev. Lett.* **63**, 2256 (1991)
- [Tung, 1984] R.T. Tung, *Phys. Rev. Lett.* **52**, 461 (1984)
- [Vartanian, 1953] A. Vartanian, “*Diderot and Descartes*”, Princeton University Press (1953)
- [Voigtländer, 2001] B. Voigtländer, *Surf. Sci. Rep.*, **43**, 127 (2001)
- [Vrijmoeth, 1994] J. Vrijmoeth, H.A. Vandervegt, J.A. Meyer, et al. *Phys. Rev. Lett.* **72**, 3843 (1994)
- [Vučković, 2000] J. Vučković, M. Lončar, A. Scherer, *IEEE J. Quant. Electr.* **36** 1131 (2000)
- [Wang, 2002a] J.-Z. Wang, J.-F. Jia, X. Liu, W.-D. Chen, and Q.-K. Xue, *Phys. Rev. B* **65**, 235303 (2002)
- [Whall, 1995] T.E. Whall, E.H.C. Parker, *J. Materials Sci; Materials in Electronics*, **6**, 249 (1995)
- [Yakes, 2004] M. Yakes, V. Yeh, M. Hupalo, and M. C. Tringides, *Phys. Rev. B* **69**, 224103 (2004)
- [Yeh, 2000] V. Yeh, L. Berbil-Bautista, C. Z. Wang, K. M. Ho, and M. C. Tringides, *Phys. Rev. Lett.* **85**, 5158 (2000)
- [Yuh, 1996] E.L. Yuh, E.G. Gwinn, P.R. Pinsukanjana, W.L. Schaich, K.L. Campman, P.F. Hopkins, and A.C. Gossard, *Phys. Rev. B* **54**, 11467 (1996).
- [Zandvliet, 1995] H. J. W. Zandvliet, H. K. Louwsma, et al., *Phys. Rev. Lett.* **75**, 3890 (1995)
- [Zeng, 2008] C. Zeng, P.R.C. Kent, T-H. Kim, A-P. Li, and H.H. Weitering, *Nature Mater.* **7**, 539 (2008)
- [Zhang, 1998] Z.Y. Zhang, Q. Niu, and C.K. Shih, *Phys. Rev. Lett.* **80**, 5381 (1998)
- [Zangwill, 1988] A. Zangwill, *Physics at surfaces*, Cambridge university press (1988)

VITA

Eun Ju Moon was born in Busan, South Korea. In 2003, after attending in Korea Atomic Energy Research Institute and Pusan National University in Korea, she started to pursue her PhD degree at the University of Tennessee, Knoxville. Eun Ju worked under the direction of Dr. Hanno H. Weitering in the area of Condensed Matter Physics. She is a member of the Sigma Pi Sigma National Physics Honor and she is coauthor of several scientific publications. The doctoral degree was received December 2009.