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This research program is aimed at studying the atomic structure of semiconductor surfaces using scanning tunneling microscopy (STM). Extensive work has been carried out on the behavior of both indium and gallium on the (111) and the (100) surfaces of silicon. The STM images provide new structural information on all of the metal-induced surface reconstructions observed in these systems. The STM has been particularly applicable to the study of multi-phase surfaces, localized defects, local metal segregation, all of which arise during the growth of a metal on a semiconductor, and can play an important role in the properties of the surface. Information on such spatially localized features (sub-100 Å) is inaccessible by other means. Some preliminary studies of the InP(110) surface have been done. It is anticipated that the primary thrust of the research will shift to compound semiconductor surfaces during the coming year.

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SCANNING TUNNELING MICROSCOPY OF SEMICONDUCTOR SURFACES

Annual Summary Report

April 1, 1987 - September 30, 1988

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SCANNING TUNNELING MICROSCOPY OF SEMICONDUCTOR SURFACES

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Abstract

This research program is aimed at studying the atomic structure of semiconductor surfaces using scanning tunneling microscopy (STM). Extensive work has been carried out on the behavior of both indium and gallium on the (111) and the (100) surfaces of silicon. The STM images provide new structural information on all of the metal-induced surface reconstructions observed in these systems. The STM has been particularly applicable to the study of multi-phase surfaces, localized defects, local metal segregation, all of which arise during the growth of a metal on a semiconductor, and can play an important role in the properties of the surface. Information on such spatially localized features (sub-100Å) is inaccessible by other means. Some preliminary studies of the InP(110) surface have been done. It is anticipated that the primary thrust of the research will snift to compound semiconductor surfaces during the coming year.

The primary goal of this research program has been to use scanning tunneling microscopy (STM) to study the structure of semiconductor surfaces, with an emphasis placed on two different areas: the behavior of metals on semiconductors (mainly silicon), and the structure of compound semiconductor surfaces. Most of the work carried out during this year focused on the first area. We have imaged many new metal induced surface reconstructions of the Si(111) surface for the first time. For the great majority of these reconstructions, little or no prior structural information was available, and the STM images revealed enough of the general nature of each structure to constrain atomic models that could be proposed. Unfortunately, in the absence of detailed theoretical calculations, it was often impossible to determine the surface atomic structure explicitly. One very important exception, however, was the In (or Ga) induced $\sqrt{3}\times\sqrt{3}$ structure where it was possible to identify the bonding site of the metal adatoms. This information confirmed a previously assumed structural model, making this particular phase the most completely understood surface reconstruction of a silicon surface. Comparison between the $\sqrt{3}\times\sqrt{3}$ and the Si(111) 7×7 structure also provided some insight into the nature of the clean Si surface.

Before proceeding with a detailed description of the work on Si surfaces, it is appropriate to summarize briefly the progress to date on the study of compound semiconductor surfaces. We have some preliminary data on the cleaved InP(110) surface which is similar to the published data on GaAs(110). Our eventual objective is to study the behavior of metals on the cleavage surfaces of both III-V and II-VI compound semiconductors. Recent theoretical work predicts different adsorption sites for different metals on GaAs(110). STM images of isolated metal atoms on the surface might be able to verify these models of adsorption. Other metals are known to be highly mobile at room temperature and to form clusters at even extremely low coverages. In these cases the STM offers the opportunity to study the behavior of very small clusters of adsorbates, and to see if the semiconductor surface between clusters is unperturbed by metal deposition. The study of adsorbed metals and defects induced on the surface by metal adsorption will be of direct relevance to other work on the initial stages of Schottky barrier height formation.

Other enhancements to the STM/ vacuum system, such as a sample entry load lock, and revised software and hardware for spectroscopic measurements, will be necessary for much of this future work. When these preparations are complete about the end of this calendar year, we anticipate shifting the bulk of the experimental effort from Si to the compound semiconductors.

Studies of Metal Induced Reconstructions of the Silicon Surface

Most of the work on metals on Si has focussed on group III metals (In,Ga). These metals are notable for inducing different surface reconstructions depending on the density of the metal on the surface. Initial work on the In/Si(111) system reported the structure of two of these phases.[1] This work has now been extended to a wider coverage range, and three new phases have been detected.[2,3,4] A similar survey of the Ga/Si(111) system has now been carried out.[5,6] Preliminary work on the Sn/Si(111) has also shown promising results. Finally, this work is being extended to the Si(100) surface.[7] The focus of the studies has now shifted away from the structure of perfect ordered surfaces to the study of multi-phase surfaces, phase boundaries, localized defects, local metal segregation. In particular, as this work is extended to the Si(100) surface, it is hoped that the results will provide insight into the nucleation and initial stages of thin-film growth in systems such as GaAs on Si(100).

Specific scientific results are summarized as follows:

1) Behavior of In on the Si(111)7×7 Surface

For the indium/silicon(111) system, we have now identified five different surface reconstructions in the range of coverages below one monolayer (ML): adatom replacement in the native Si 7×7 pattern at less than 0.1 ML, the $\sqrt{3}\times\sqrt{3}$ structure at 0.3 ML, the $\sqrt{31}\times\sqrt{31}$ at 0.6 ML, and two phases, 4×1 and c2×4, coexisting between 0.75 and 1 ML. The behavior at low coverage is of particular interest since the bonding arrangement of the In adatoms in either the 7×7 or the $\sqrt{3}\times\sqrt{3}$ structures is directly identified in the STM images. As mentioned previously, the determination of the metal atom bonding site in the $\sqrt{3}\times\sqrt{3}$ arrangement makes this the first metal induced reconstruction to have a detailed atomic structural model that is understood on both an experimental and theoretical basis. The In atoms lie on the threefold sites above second layer Si atoms, a location referred to as T_4 in recent literature. This result confirms a theoretical prediction that this is the lowest energy site for a group-III metal adatom in the $\sqrt{3}\times\sqrt{3}$ arrangement. We have also identified the same structure for the Ga/Si, and expect the same behavior in the Al/Si system studied by *Hamers et al.* at IBM.

Some of these results were reported at the 15th Conference on the Physics and Chemistry of Semiconductor Interfaces (PCSI-15) at Asilomar Ca, in February 1988.

2) Ga Induced Reconstructions of Si(111)

The STM images show that up to 0.7 ML coverage, there are two new surface phases that occur. At low coverage, the behavior of Ga is identical to In, with Ga adatom replacement in the native 7×7 structure. The first new phase is at 1/3 ML which is the $\sqrt{3}\times\sqrt{3}$ reconstruction. The STM images confirm the same structure and metal bonding site as in In/Si(111). At higher coverage, a new incommensurate phase is seen which corresponds to a 6.3 x 6.3 RHEED pattern reported in the literature. This high coverage phase consists of well-ordered triangular subunits arranged in a quasi-periodic manner across the surface. The structure within the sub-units appears to be 1x1, in registry in the bulk Si lattice positions. This is the first observation of an incommensurate surface reconstruction in any of the systems that we have studied. These images may provide some insight into the general nature of incommensurate surface phases that have been seen in other metal/Si systems. The only other analogous structure that has been seen by STM is the Cu/Si(111) 5x5 which has been reported very recently by IBM.

These results were reported at the 3rd International Conference on Scanning Tunneling Microscopy at Oxford England, in July 1988.

3) Behavior of Sub-monolayers of Sn on Si(111)

The structure of different reconstructions of tin on Si(111) has been studied. Tin (Sn) is of interest because it has been shown to grow with some degree of epitaxy on both Ge and Si substrates. Since Sn is just below Si and Ge in the periodic table, it might be expected that the surface reconstructions induced by Sn on Si might be very similar to those of clean Si or Ge. It has been demonstrated that a "normal" 7×7 structure can exist on Sn/Ge alloys. However, we find that deposition of Sn on Si produces new structures that are not seen on bare Si. For less than a monolayer (ML) of Sn, three different reconstructions are seen with 7×7, $\sqrt{3}\times\sqrt{3}$, and $2\sqrt{3}\times2\sqrt{3}$ periodicities. The 7×7 structure has the same unit cell as that of the clean surface but there is obvious disruption of the adatom structure. The $\sqrt{3}\times\sqrt{3}$ phase is a 1/3 ML array of adatoms similar to that of Al, Ga, or In on Si(111). The registration of adatoms at 7×7 / $\sqrt{3}\times\sqrt{3}$ phase boundaries indicates that the adatoms in the $\sqrt{3}\times\sqrt{3}$ structure lie in the threefold sites above second layer Si atoms. The $2\sqrt{3}\times2\sqrt{3}$ structure is shown to be two-fold symmetric with the three orientations on the surface giving the threefold symmetry apparent in the LEED pattern. All three surface phases are shown to coexist above 0.3 ML. Adatom trimers are seen on some 7×7 unit cells, suggesting a new structure that may be a prelude to the formation of the $\sqrt{3}\times\sqrt{3}$ phase.

4) Ga on Si(100)

We have now discovered appropriate surface cleaning procedures for Si(001), and we have proceeded to extend our work on metal induced reconstructions to this new substrate surface. The first results concern the Ga/Si(001) system. This system is of particular interest because of the relevance to heteroepitaxial growth of GaAs on Si(001). Although most GaAs growth starts with a surface terminated by As rather than Ga, it has been shown that the behavior of Ga on the surface is crucial in the nucleation of growth on the surface. In addition it has been demonstrated that a Ga predeposition procedure can influence GaAs island size distribution in thin, discontinuous GaAs films. Control of the initial stages of growth is important because defects that form from the beginning, such as anti-phase domains, can propagate through the GaAs film and have a strong effect on its bulk properties.

The initial results on this system focus on low metal coverages where the effects of the substrate surface are strongest, and the nucleation of growth can be studied in some detail. The Ga atoms are much more mobile than on the Si(111) surface under the same conditions. At low metal density (0.07 ML), the Ga atoms have a strong tendency to order in rows on the surface, parallel to the Si dimerization direction. As a result, areas covered by Ga are strongly elongated in <110> type directions. As the metal density is increased, these rows form local areas of 3×2 order. Where a step is present, metal growth tends to nucleate on the lower terrace edge, but is not necessarily confined to areas near the step. The steps do not appear to affect strongly the one-dimensional character of the growth.

Instrumental Development

Instrumental development has followed two tracks. The first has been to enhance the sample handling and preparation facilities of the existing system. The second has been to develop a new STM stage, based extensively on the current design with the additional capability of switching tunneling tips in vacuum.

We have added the capability of cleaving single crystals to our STM/ vacuum chamber system. The cleaver has been used in a preliminary experiment on the cleaved surface of InP. The further addition to the chamber of a fast sample entry load lock is anticipated this fall. This will allow the introduction of samples that cannot be baked during the initial pumpdown of the vacuum system. Such samples could include As-capped MBE grown GaAs wafers, and various Hg, Cd and Zn-containing II-VI semiconductors. We will also be revising both hardware and software to enable the taking of localized I-V curves over the surface which will be important in studying localized defects or metal clusters on the surface.

We have almost completed the construction of the second generation microscope. The major advantage of the new design is the capability of switching tunneling tips without breaking vacuum. This addresses the major bottleneck in our current STM experiments which has been the limited lifetime of the tip. Until this new instrument is on line, changing the tip will always involve venting the vacuum system, which then implies a three day turnaround period in order to recover ultra-high vacuum conditions. Up to eight tips are stored at a time in the STM flange itself, and are readily transferrable to the PZT scanner *in vacuo*. It will also be possible to transfer tips to the microscope from outside the chamber via a fast sample entry load lock, and to hold the tips in the existing sample manipulator in order to evaluate tip cleaning procedures in vacuum, safely away from the STM stage itself. Other changes have been made to simplify the operation and maintenance of the instrument, but the basic configuration is not changed from the current proven design. It is anticipated that this new STM will be in operation by the end of this calendar year

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[1] "Indium-induced reconstructions of the Si(111) surface studied by scanning tunneling microscopy," J. Nogami, Sang-il Park, and C.F. Quate, Phys. Rev. B **36**, 6221-6224 (1988)

[2] "Scanning Tunneling Microscopy: Instrument design and application in air and vacuum," Sang-il Park, J. Nogami, and C.F. Quate, *Proceedings of the SPIE* volume 897, 8-15 (1988)

[3] "Structure of the 4×1 and $\sqrt{7} \times \sqrt{3}$ surface reconstructions of In on Si(111) studied by scanning tunneling microscopy," Sang-il Park, J. Nogami, and C.F.Quate, (submitted for publication)

[4] "Behavior of Indium on the Si(111)7×7 Surface at Low Metal Coverage," J. Nogami, Sang-il Park, and C.F. Quate, J. Vac. Sci. Technol. B **6**(4), 1479-1482 (1988)

[5] "An STM Study of the Gallium Induced $\sqrt{3}\times\sqrt{3}$ Reconstruction of Si(111)," J. Nogami, Sang-il Park, and C.F. Quate, Surf. Sci. 203, L631-L636 (1988)

[6] "Metal induced reconstructions of the silicon (111) surface," Sang-il Park, J. Nogami, and C.F. Quate, *Proceedings of the 3rd Int. Conf. on STM, Oxford '88*

[7] "Behavior of Ga on Si(100) as Studied by Scanning Tunneling Microscopy," J. Nogami, Sang-il Park, and C.F. Quate, (submitted for publication)

Other Publications:

[8] "Chemical Dependence of the multiple-tip effect in scanning tunneling microscopy," Sang-il Park, J. Nogami, H.A. Mizes, and C.F. Quate, Phys. Rev. B (in press)

Attached is our Publications/Patents/Presentations/Honors Report for 1 October 1987 through 30 September, 1988.

June 1988

OFFICE OF NAVAL RESEARCH

PUBLICATIONS / PATENTS / PRESENTATIONS / HONORS REPORT

FOR

1 OCTOBER 19 87 through 30 SEPTEMBER 1988

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CONTRACT N00014 - 87-K-0679

R&T NO. 4127057

TITLE OF CONTRACT: Scanning Tunneling Microscopy of Semiconductor Surfaces

NAME(S) OF PRINCIPAL INVESTIGATOR(S) C. F. Quate

NAME OF ORGANIZATION: Stanford University

ADDRESS OF ORGANIZATION: Edward L. Ginzton Laboratory
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June 1988

PAPERS SUBMITTED TO REFEREED JOURNALS
(Not yet published)

"Characterization of Gold Surfaces for Use as Substrates in Scanning Tunneling Microscopy Studies"
R. Emch, J. Nogami, M.M. Dovek, C.A. Lang & C.F. Quate
G.L. Report No. 4361 (April 1988, revised August 1988)
Submitted to Journal of Applied Physics
Partially supported by the Defense Advanced Research Projects Agency

"Behavior of G- on Si(100) as Studied by Scanning Tunneling Microscopy"
J. Nogami, Sang-il Park & C.F. Quate
G.L. Report No. 4383 (July 1988)
Submitted to Applied Physics Letters
Partially supported by the Defense Advanced Research Projects Agency

"Metal Induced Reconstructions of the Silicon (111) Surface"
Sang-il Park, J. Nogami & C.F. Quate
G.L. Report No. 4391 (July 1988)
To be published in the Journal of Microscopy
Partially supported by the Defense Advanced Research Projects Agency and the Joint Services Electronics Program

"Characterization and Local Modification of Atomically Flat Gold Surfaces by STM"
R. Emch, J. Nogami, M.M. Dovek, C.A. Lang & C.F. Quate
G.L. Report No. 4424 (September 1988)
To be published in the Journal of Microscopy
Partially supported by the Defense Advanced Research Projects Agency

June 1988

PAPERS PUBLISHED IN REFEREED JOURNALS

"Behavior of Indium on the Si(111)7x7 Surface at Low-Metal Coverage"
J. Nogami, Sang-il Park & C.F. Quate
J. Vac. Sci. Technol. B, 6(4), 1479
(Jul/Aug 1988)

"An STM Study of the Gallium Induced $\sqrt{3}x\sqrt{3}$ Reconstruction of Si(111)"
J. Nogami, Sang-il Park & C.F. Quate
Surface Science, 203, L631 (1988)

June 1988

PAPERS PUBLISHED IN NON-REFEREED JOURNALS

NONE

June 1988

TECHNICAL REPORTS PUBLISHED

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BOOKS (AND SECTIONS THEREOF) SUBMITTED FOR PUBLICATION

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BOOKS (AND SECTIONS THEREOF) PUBLISHED

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INVITED PRESENTATIONS AT TOPICAL OR
SCIENTIFIC/TECHNICAL SOCIETY CONFERENCES

See attached sheet

HONORS/AWARDS/PRIZES

1988 IEEE Medal of Honor for "The invention of the Scanning Acoustic Microscope" received at the IEEE Annual Medals Presentation and Reception, Sheraton Boston Hotel, Boston, Massachusetts, May 9, 1988.

INVITED PRESENTATIONS

C. F. Quate, "Surface Tunneling Microscopy," Fourth Annual Science & Technology Seminar 'Advances in Catalytic Technologies', Catalytica, San Jose, California, October 26, 1987

Sang-il Park, "Scanning Tunneling Microscopy: Instrument Design and Application in Air and Vacuum," SPIE-Society for Optical Engineering Meeting 'Scanning Microscopy Technologies and Applications', Los Angeles, California, January 13-15, 1988

C. F. Quate, "Molecular Imaging with the STM and the AFM," International Symposium on Surface Interactions, Neve Ilan, Jerusalem Hills, Israel, March 13-18, 1988

C. F. Quate, "Acoustic Microscopy - Historical Aspects," International Research Conference on Ultrasonic Micro-Spectroscopy for Material Characterization (UMS), Sendai, Japan, June 6-8, 1988

C. F. Quate, "Imaging with the STM and the AFM," International Conference on Solid State Devices and Materials (SSDM), Tokyo, Japan, August 24-26, 1988

CONTRIBUTED PRESENTATIONS

J. Nogami, "Behavior of Indium on the Si(111)7x7 Surface at Low Metal Coverage," 15th Annual Conference on the Physics and Chemistry of Semiconductor Interfaces (PCSI-15), Asilomar, February 1-4, 1988

Sang-il Park, "Indium Induced Reconstructions of Si(111) Studied by Scanning Tunneling Microscopy," 1988 March Meeting of the American Physical Society, New Orleans, March 21-25, 1988

Sang-il Park, "Metal Induced Reconstructions of the Silicon (111) Surface," 3rd International Conference on Scanning Tunneling Microscopy, Oxford, England, July 4-8, 1988.

June 1988

GRADUATE STUDENTS SUPPORTED UNDER
CONTRACT FOR YEAR ENDING 30 SEPTEMBER 19 88

T. R. Albrecht

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POSTDOCTORALS SUPPORTED UNDER
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J. Nogami

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