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固体表面と界面のトピックスに
関する国際会議

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THE INTERNATIONAL TOPICAL
CONFERENCE
ON
SOLID SURFACES AND INTERFACES
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THE SURFACE SCIENCE SOCIETY OF JAPAN

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この国際会議は、その直前に東京で行われた本学会と
応用物理学会との共催による MBE-CST-2 (The 2nd
International Symposium on Molecular Beam Epitaxy
and Related Clean Surface Techniques, 27-30, Au-
gust, 1982) の開催を前にして、1982年8月25、26の両
日東京農工大学において開催されたものである。

講演の題目と内容の抄録は以下に示す如きものであ
った。講演はいずれも本学会による招待講演であり、表面
および界面の構造、形成過程、評価、分析等について最
も新しい成果の一端を紹介するものであり、聴衆に多く
の感銘を与えた。世界各地から、すぐれた第一線の研究
者を講演者として得て研究講演会を開くことができたこ
とは幸せであった。

STUDIES OF FOREIGN ATOMS ON THE
SURFACES OF SOLIDS ION BEAM
AND X-RAY STANDING WAVE
TECHNIQUES

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One of the important questions in understanding

the interaction of foreign atoms with the surface of
a single crystal solid is: "Where are the atoms?".
This refers to atoms in the surface layers of the
substrate crystal as well as adsorbed foreign atoms.
In recent years a number of new techniques have
been developed to answer this important question.
This paper will review two of these; High Energy
(MeV), Ion Scattering and X-Ray Standing-Wave
interference Spectroscopy. Ion channeling has been
known for almost twenty years but it is only dur-
ing the past few years that it has been applied to
studies of surface and interface structure. Adsorbate
induced substrate crystal reconstruction and relaxa-
tion is illustrated by oxygen adsorbed on a Ni(111)
surface⁽¹⁾. Structural changes during the early stages
of epitaxial growth are illustrated using germanium
on Si(111)⁽²⁾ and the power of transmission chan-
neling through thin films is demonstrated for pal-
adium on a Si(111) surface⁽³⁾. X-Ray Standing
Wave Interference Spectroscopy (XSWIS) is a very
new technique capable of measuring the position of
foreign atoms with a precision of $\sim 0.02 \text{ \AA}$ with a
sensitivity of < 0.1 monolayers. The principles of
this technique are reviewed and studies of bromine
adsorbed on Si(110) and Si(111) surfaces from
methanol solution are described⁽⁴⁾. The unique
ability of this technique to determine foreign atom
positions at solid-solid, solid-liquid and solid-gas as
well as solid-vacuum interfaces is demonstrated.
This work was supported by The Office of Naval
Research under Contract # 0014-78-c-0616.

- (1) Phys. Rev. Lett. **47** 417 (1981); Surface Sci. **114** 331 (1982).
- (2) Phys. Rev. Lett. **47** 1459 (1981); J. Vac. Sci. Technol. **20** 709 (1982).
- (3) J. Vac. Sci. Technol. **20** 869 (1982).
- (4) J. Vac. Sci. Technol. **20** 634 (1982).

THE INTERFACE OF GaAs(001) AND Al

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The formation of an interface of MBE-grown
GaAs(001) and Al has been analyzed by AES and
RHEED. The subsequent electrical characteristics
of the formed Schottky barrier was studied by CV-
and IV-techniques. All experiments were performed
in a Varian MBE-360 system.

The magnitude of the Al-LVV transition was
studied in the monolayer (ML) range for growth on
GaAs(001) $c(4 \times 4)$, $c(2 \times 8)$ and (4×6) surfaces.
Measurements were performed in the temperature
range 268 K to 673 K. The Al growth was charac-
terized by an initial linear increase preceding the

nucleation which strongly depended on the temperature. At high temperatures, 523 K for $c(2 \times 8)$ and 400 K for (2×6) , no nucleation was observed.

The Schottky barrier formed exhibited no dependence of the barrier height on the initial surface reconstruction (i.e. As/Ga-ratio). Upon annealing the interfaces an interface layer is formed. The composition of this interface is discussed based on the annealing behaviour of the Schottky barrier.

THE GROWTH OF METALS ON III-V SEMICONDUCTORS

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In the last few years, a great experimental effort has been devoted to the study of the epitaxial growth of thin metal films on III-V semiconductors. A review of the main results obtained by the different groups active in the field is given with special emphasis on surface and interface related features. In general, metals were deposited onto semiconductor surfaces according to an MBE process. Moreover, most of the results were obtained on GaAs {001} epitaxial layers grown in situ by MBE.

However, some results concerning GaAs {001} surfaces prepared by ion bombardment and annealing (IBA) or GaAs {011} surfaces obtained by cleavage, as well as other III-V semiconductors such as InP and InSb are also available. Very different metals have been grown epitaxially on III-V semiconductor surfaces: Al, Ag and Au on GaAs and InP {001} surfaces, Fe on GaAs {011} and {001} surfaces and Sn on InSb {001} surface. Various epitaxial relationships exist between these metals and the semiconductor surface, depending on the following main parameters:

- 1 - temperature of the growth
- 2 - surface reaction between metal and semiconductor
- 3 - misfit between the two lattices
- 4 - structure of the metal (i.e. fcc, bcc.)

One of the most striking characteristics of the metal epitaxial layers is that surface reconstructions are often observed, in particular for Al and Ag grown onto GaAs {001} surfaces, while such reconstructions are not known as intrinsic surface properties of standard metal single crystals. Another important observation is that the difference between the two $\langle 110 \rangle$ axis with respect to the dangling bonds direction at the surface, induces profound anisotropic effects in the metal layer, as clearly indicated by recent synchrotron radiation plane wave experiments. After discussing the main features of the growth of metals over semiconductor surfaces, some new results will be given on the

growth of semiconductor/metal/semiconductor structures which involves severe difficulties, but which are obviously of great potential interest for both fundamental and practical purposes.

ELECTRONIC AND CRYSTALLOGRAPHIC STRUCTURE OF MBE-GROWN GaAs SURFACES

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The application of molecular beam epitaxy (MBE) techniques makes it possible to prepare a wide range of clean, damage-free, reconstructed surfaces of III-V semiconductors, which can then be examined in situ to evaluate their composition, crystallographic and electronic structure. We have combined MBE with reflection electron diffraction (RHEED), synchrotron radiation excited angle-resolved photoemission (ARPES) and core-level photoemission to investigate various reconstructions of, and metal overlayers on, the technologically important (001) GaAs surface.

The different reconstructions are related to its variable stoichiometry, with the 2×4 and $c(4 \times 4)$ structures being generally considered as As-rich, the latter having the higher As-coverage, while 4×2 and 4×6 structures have higher Ga concentrations. The driving force for the 2×4 reconstruction, which is the most stable, appears to be the formation of an asymmetric As-As dimer bond between adjacent As surface atoms. This gives rise to a nearly dispersionless state ≈ 3 eV below the VBM, while dangling bond states with significant in-plane character are found in the energy range near the top of the projected bulk bands. The dimer related state is absent in the $c(4 \times 4)$ surface, and also in surfaces with sub-monolayer coverages of certain metals (e.g. Pb). In addition it has been possible to deduce from RHEED patterns that the reconstructed surfaces are not totally ordered, but show evidence of a domain structure in one of the orthogonal $\langle 110 \rangle$ directions. There is also some evidence that deep level incorporation in MBE-grown films may be related to surface structure.

INTERFACE STRUCTURE OF Si FILMS GROWN BY ION-ENHANCED TECHNIQUES

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Ion beam sputtering (IBS) and partially ionized vapor deposition (PIVD) have been applied to prepare crystalline and amorphous silicon films [1, 2]. Structure investigations in conjunction with measurements of electrical and photoelectronic properties revealed that the layers exhibit specific features that must be ascribed mainly to defects produced at the interface and within the growing films by the action of energetic ions and neutrals. The principal results may be summarized as follows:

Epitaxial films on silicon and spinel substrates were obtained by ion beam sputtering with Ar^+ at 6...10 keV in the temperature region from 800...1000°C. A detailed analysis of thinned specimens by transmission electron microscopy (TEM) showed, however, that the films contain numerous defects, in particular stacking fault arrays, twinned regions, dislocations and agglomerations of point defects. In the early stage of film growth the formation of defects was detected even on the uncovered substrate surface regions between threedimensional islands. Hence the impinging energetic ions and neutrals are made responsible for the defect creation. Increased substrate temperatures resulted in lower defect concentrations, but then other extended defects originating from β -SiC particles were observed.

Stepwise thinning of the films by chemical respectively ion beam etching enabled to determine the Hall mobilities differentially. It was found that the mobilities decreased linearly within a 3 μm thick transition region, and became negligibly small near the interface of heteroepitaxial samples.

Investigations of films grown by PIVD confirmed that the participation of accelerated ions in the deposition process causes increased defect densities particularly near the substrate/film interface.

Amorphous hydrogenated silicon films (a-Si:H) were prepared by ion beam sputtering at substrate temperatures from 100...450°C. The hydrogen was supplied either by the residual gas or—more efficiently—by feeding a gas mixture of Ar/H_2 to the sputter ion source. Depending on the deposition parameters the hydrogen content and the band gap could be varied within wide limits, however, the defect concentrations remained for most of the samples to high to accomplish effective doping.

The observed photocurrents were often found to be lower than the dark-currents.

In accordance with the highly disturbed structure extremely low recombination times for these a-Si:H films were found by picosecond reflectivity measurements using double pulses of modelocked Nd:YAG lasers. Moreover, it could be demonstrated that the relaxation time can be adjusted within about three orders of magnitude down to a few picoseconds, eventually even to smaller values, by varying the deposition parameters.

Another prospective application is offered by using the amorphous films prepared by IBS as transition layers for graphoepitaxial refilms prepared by IBS as transition layers for graphoepitaxial recrystallization. Comparative investigations indicated that the perfection of recrystallized layers obtained from ion-beam-sputtered layers is superior to that prepared from other types of a-Si:H.

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/2/ C. Weissmantel, K. Bewilogua, D. Dietrich, H.-J. Erler, H.-J. Hinneberg, S. Klose, W. Nowick and G. Reisse, Thin Solid Films, 72 (1980) 19.

THE EXTRAORDINARY STRUCTURE SENSITIVITY OF THE ADSORPTION OF O_2 AND CO ON (111) Pd

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Almost all previous surface studies on (111) Pd have been carried out using sputter etched and annealed bulk crystals. These investigations have shown that O_2 and CO form ordered superlattices at relatively low gaseous exposures and that the (111) Pd surface will actively catalyze the oxidation of CO at rates that depend upon the experimental conditions. In the present study vacuum deposited Pd films were used for similar studies. These films were formed in two ways: (1) on (111) Cu films that had been deposited epitaxially on thin (111) NaCl films formed on mica; and (2) directly on mica. The epitaxial growth of these Pd films was studied by AES, LEED, RHEED, TEM/TED, and replica TEM techniques. The AES investigations included both Auger intensity and R-factor measurements. It was found that (111) Pd grows on (111) Cu at 25°C by a monoatomic layer growth mechanism and that $\sim 1500 \text{ \AA}$ thick (111)Pd films formed on mica also grow by layer growth. These

surfaces along with those of polycrystalline Pd film were exposed to 6000 L of O₂ and 7200 L of CO. The surface oxygen and CO concentrations were determined by AES methods. Surfaces contaminated with Cl (from NaCl) adsorbed the largest amounts of O and CO. Much less O and CO were adsorbed on polycrystalline Pd surfaces while very little was adsorbed on a somewhat rough (~800 Å thick) (111) Pd monocrystalline surface. The most striking result of all was the observation that at 25°C the clean, thick (~1500 Å), flat (111) Pd surface does not adsorb O or CO at all.

EXTENDED FINE STRUCTURE ANALYSIS OF LOW-Z ADSORBATES*

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The application of extended fine structure analysis to the determination of local structure associated with a particular elemental constituent is severely restricted by the problem of overlapping absorption edges. To accurately determine interatomic separations, extended fine structure must be analyzed for several hundred volts above an edge. If an absorption edge of a different element falls within this region, analysis by conventional techniques is not possible. This limitation has been particularly severe in surface techniques such as SEXAFS and EAPFS, since surface studies tend to concentrate on the important case of low-Z adsorbates, and the problem of overlapping edges is most severe for low-Z elements in the presence of relatively high-Z elements. To avoid this difficulty, we have recently developed a technique that utilizes the electron-excited Auger spectrum of an element to monitor the core-level excitation probability. Using this technique, we have shown that it is possible to analyze extended fine structure above the oxygen 1-s edge, even though this edge falls between the titanium 2-p and 2-s edges. The technique has also been applied to the study of monolayer quantities of sulfur on titanium. All measurements were performed using a standard cylindrical mirror Auger spectrometer.

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ARUPS OF MBE-GROWN GaAs (001)

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Surfaces of GaAs(001) were prepared by Molecular Beam Epitaxy (MBE). Surface geometries were de-

termined by electron diffraction (RHEED) before the samples were transferred into a separate surface analysis system via a UHV interlock system. Surface studies were here undertaken by LEED and angle resolved ultraviolet photoelectron spectroscopy (ARUPS) at 16.8 and 21.2 eV. The c(4×4) and c(2×8) surface reconstructions were initially prepared in the MBE-system. The c(2×8) and (4×6) surface structures were formed by annealing in the vacuum system. Electron energy spectra were measured at different polar angles using UPS. Experimental spectra have been compared to transitions predicted by bulk band calculations. Surface induced features in spectra will be discussed.

DETERMINATION OF SURFACE STRUCTURES BY ANGLE-RESOLVED PHOTOEMISSION SPECTROSCOPY

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Angle-resolved photoemission spectroscopy contains surface structural information due to diffraction of the photoelectron by neighbors of the emitting atom.

Two modes of measurement are usually employed: (1) Photoelectrons from a fixed (initial) level are collected at fixed exit angle as a function of varying photon energy, and (2) photoelectrons at a fixed photon energy are collected as a function of exit angle. Structural information most readily determined are surface layer spacings and orientation of local surface complexes. Special features of the technique are: (1) The probe is site specific and (2) it requires only local ordering of length comparable to the electron mean-free-path.

Applications of this technique to atomic and molecular adsorption are given. Also, we compare this technique to surface EXAFS.

CALCULATIONS OF RHEED

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A theory will be described which allows accurate calculations of elastic scattering intensities in Reflection High Energy Electron Diffraction (RHEED) (1, 2). The basis of the method is an expansion of the wave function in a Fourier series in the direction parallel to the surface with coefficients which depend on the co-ordinate perpendicular to the surface. After manipulation a set of integral equations is obtained from which, using appropriated boundary conditions, reflection and transmission coefficients

for a slab can be obtained. Fast computation is possible and the results can be checked using flux conservation. The results for 20 keV electrons scattering from three surfaces of Ag, (001), (110) and (111), will be presented in the form of rocking curves. These contain a great deal of structure which can be identified as primary and secondary Bragg diffraction peaks and resonance peaks. The dependence of the rocking curves on azimuth of incidence will be described. It will be shown that the RHEED pattern is very sensitive to surface structure such as the spacing of the topmost atomic layers. It will also be demonstrated that the method can be applied to calculate elastic intensities for much lower energy electrons. It can be made to work in the LEED range, though it is inefficient there, but works well in the MEED range. The results suggest that experiments using electrons in the 5-10 keV range may have significant advantages over those of higher or lower energies, with much of the sensitivity and computational advantage of RHEED but without some of the apparent experimental problems of the higher energy.

(1) P. A. Maksym and J. L. Beeby, *Surface Science* 110 423 (1981)

(2) P. A. Maksym and J. L. Beeby, *Applications of Surface Science* (to be published)

VERY LOW ENERGY ELECTRON DIFFRACTION FROM SURFACES

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Very low energy electron diffraction (0-30 eV) studies on clean and adsorbate covered surfaces are reviewed. One of the most useful surface properties which can be found by this technique is the shape of the surface barrier potential which can be deduced from the "Rydberg-series" of peaks found in these spectra. A comparison of theoretical and experimental methods is given, including a discussion of polarised electron diffraction and the extent to which surface structure can be determined.

FORMATION PROCESS OF SI-METAL INTERFACES STUDIED BY MEV HE⁺ ION SCATTERING

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A number of experiments have shown that deposited metal films intermix readily with silicon substrate at the interfaces to lead to alloyed interface formation at low temperatures ($\leq 200^\circ\text{C}$). Since silicon is a typical covalent semiconductor with large

bond energy which is $\sim 2\text{ eV/bond}$, without the presence of such an effect of metal as to modify or weaken the covalent bonding of silicon adjacent to the metal the above interfacial reaction can hardly occur.

In this respect recently Hiraki* has proposed a model postulating electronic screening of Coulomb interaction responsible for the covalent bonding of silicon crystal due to mobile free electrons in the deposited metal. This screening model seems to be evidenced at least for Si-Au system by several electron spectroscopic studies done on the initial stage of the interfacial intermixing reaction between silicon substrate and deposited Au-film under ultra high vacuum. Namely, these studies have indicated that for the intermixing reaction at the Si/Au interface to take place the Au-film thickness must exceed a critical value. This presence of the critical film thickness is understood to be necessary for the thicker Au-film than this thickness to act as an intrinsic Au-metal.

The present talk demonstrates the usefulness of MeV He⁺ ion scattering, a powerful complementary method for electron spectroscopies, to study the initial stage of Si-Metal interfacial reaction, especially the presence of the critical thickness, a key point for the screening model. The scattering experiments were done on Si-Au and Si-Pd systems by Hiraki, Narusawa and Gibson under the auspices of Osaka University and the State University of New York at Albany (SUNYA) using Dynamitron accelerator at SUNYA.

Reference

* A. Hiraki: *J. Electrochem. Soc.*, 127 (1980) 2662

MICROCLUSTERS AND COALESCENCE IN THIN FILM GROWTH

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A common mode of thin film growth is the Volmer-Webber (or 3-dimensional particle growth) mode. Recent measurements on such a system where gold is deposited onto NaCl surfaces have produced evidence that under most conditions the growth of visible clusters does not take place primarily through the addition of single atoms [1]. It is only at the lowest temperatures investigated (-150°C) that the observations are consistent with the growth occurring by single atom additions and this leads to randomly oriented f.c.c. crystals forming a highly polycrystalline film. At higher temperatures the evidence suggests that microclusters of atoms form

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but these are so mobile on the surface that growth of the larger particles in the deposit occurs predominantly through capture of these microclusters. Within such microclusters the atoms will be packed in the highest binding energy configuration which for very small clusters is not the f. c. c. structure of bulk gold [2]. Thus at these higher temperatures the structure of the larger growing particles will depend upon whether there is sufficient thermal energy available to dissociate the microclusters into independent atoms which can take up the conventional f. c. c., or even the multiply-twinned particle,

forms. At still higher temperatures there is evidence to suggest that the larger particles themselves become mobile and coalesce with or without recrystallisation depending on available thermal energy. The evidence presented consists of measured nucleation and growth kinetics together with bright and dark field electron microscopy and diffraction.

[1] B. F. Usher and J. L. Robins, *Thin Solid Films* **90**, 15 (1982).

[2] M. R. Hoare and P. Pal, *J. Crystal Growth* **17**, 77 (1972).