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Characterization of Semiconductor Surfaces and Interfaces by High Energy Ion Scattering

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The use of surface peak, which appears in MeV ion channeling experiments, is demonstrated as a local probe for direct and quantitative measurements of atomic displacements smaller than ~0.1 Å. The atomic structures of GaAs(001)-c(4x4) clean surface and hydrogen-adsorbed (lx1) surface are analyzed by this technique as well as the interface atomic structures of GaAs(001)-SiO_x and Si(111)-Pd systems.

Although enormous efforts have been devoted to the study of semiconductor surfaces, exact atomic structures are not known even in the simplest case. For instance, the GaAs(001) surface exhibits a variety of reconstruction patterns depending on the As coverage and other preparation conditions1), however the definite structure model has never been proposed. The theoretical work has been mostly limited to the ideal unreconstructed surface because of the lack of information on the positions of the surface atoms²). As for the interface beneath the surface layer, there are only few reports because most electron diffraction and spectroscopic methods are limited by the electron escape depth.

Combined with the channeling technique, high energy (~MeV) ion beams offer an extremely fine and well-characterized probe which is sensitive to lattice strain and dynamics. Since Bogh3) first demonstrated the use of such a probe for atomic structure analyses of crystal surfaces and interfaces, many works have been done. The principles, techniques, and various applications are summarized in a recent monograph by Feldman et al⁴⁾. In brief, as a result of very small shadow cone radius for MeV ions scattered by a target atom, we can determine, in principle, 3dimensional coordinates of the target atom with an accuracy better than 0.05 Å. Further, since channeled ions are likely to be steered by the atomic rows more or less towards the center of channel, the our technique is selectively sensitive to displaced atoms at the surface or interface.

The present paper demonstrates the feasibility of our technique by describing some computational and experimental results about one of the reconstructed surface structures of GaAs (001), i.e. the As-stabilized c(4x4) structure, and some interfacial structures of the Si-Pd and GaAs-SiOx systems.

Our experimental apparatus (Fig.l) consists of an MBE system, which has four sets of conventional Knudsen effusion cell, and a UHV ion scattering chamber, which is connected to a Pelletron accelerator via beam collimating and differential pumping stage. The scattering chamber, also equipped with LEED and PIXE systems, is connected to the MBE system through an isolation valve, and the samples are transfered from each to another without exposing to the air. The scattered ions are detected by a Si detector of surface barrier type ($\Delta E \sim 15 \text{ keV}$), which is mounted on a rotatable stage to make possible to change the scattering angle of detected particles.

Figure 2 displays the $\langle 001 \rangle$ alinged spectra in the conventional backscattering mode (a) and the grazing exit-angle mode (b). Simply because of a longer travelling distance of scattered particles in (b) than in (a), the surface sensitivity gets much increased in (b) and we can clearly seperate the particles scattered by the surface from those by the bulk. Indeed, the peak at the highest energy in Fig.2 (b) corresponds to scattering by the surface atoms and refered to the surface peak (SP). The SP intensity is very sensitive to subtle displacements or relaxation of the surface atoms as well as the surface dynamics.

Experimental SP intensities are sometimes compared with computer simulation, which is necessary to derive any quantitative conclusions in our case because there exists no simple analytical method to estimate realistic SP



Fig. 1 Schematics of an MeV ion scattering - MBE combined system.



Fig. 2 Scattering geometry and typical aligned spectra from GaAs target. (a) Conventional backscattering mode, and (b) grazing exit-angle mode.

intensities. On the basis of the classical binary collision model, the nuclear encounter probability⁵) can be calculated by the Monte Carlo simulation method assuming the position and the thermal vibration amplitude of surface atoms at will.⁶)

Figure 3 shows calculation results of scattering probabilities for 2 MeV He⁺ ions impinging upon a string of As atoms. The interatomic distance along the beam direction, d, and the root-mean-square one dimensional thermal vibration amplitude, u₁, are assumed to be the same as those of As atoms in the GaAs bulk crystal, i.e. d= 4.00 Å in the $\langle 110 \rangle$ direction and u₁ = 0.093 Å. The scattering probability is unity of course for the first atom in the string, and decreases steeply for underlying atoms due to the shadowing effect. The SP intensity corresponds to the sum of all of these probabilities and expressed conventionally in units of atoms/string or





atoms/row, which is the number of atoms per string effectively contributing to the scattering of He⁺ ions. The sensitivity of 1 MeV - $\langle 001 \rangle$ SP intensity to surface atomic displacements is shown in Fig.4. As a function of the lateral displacement distance, x, of the first Ga atom, the SP intensity increases monotonically and saturates at x ~ 0.25 Å, which agrees approximately with the shadow cone radius, R_C = 2 (Z₁ Z₂ $e^{2d/E})^{1/2} \sim 0.142$ Å for the coulombic potential, plus u₁ ~ 0.089 Å. Here, E is the incident energy, Z₁ and Z₂ are the atomic number of projectile and target atoms, respectively.

High energy ion scattering has been applied to many surface structure analyses, however the systems studied so far4) are mostly limited to Si or metal surfaces and there is no report about the practically important GaAs(001) surface. This is probably because controlled preparation of this surface is difficult by conventional techniques like thermal flashing or rare gas ion bombardment. The GaAs(001)-c(4x4) surface in the present study was prepared by MBE growth at Subsequent ~ 500°C on n-GaAs(001) substrates. exposure of the c(4x4) surface to hydrogen gas of 1x10-6 Torr for \sim 10 min at room temperature gave a sharp (lxl) pattern suggesting relaxation of the reconstruction has occurred. Figure 5 shows typical $\langle 001 \rangle$ aligned spectra for the c(4x4) structure (a) and (1x1) structure (b) as compared with the random spectrum (c) from a reference target, which is a Si wafer with As implanted by 1.0×10^{16} cm⁻². Due to a limited energy resolution of the detector and also due to our relatively small scattering angle of ~95 deg., the spectra in Fig.5(a) and (b) do not allow discrimination between Ga- and As-surface atoms. This problem can be overcome by utilizing better mass-discriminating technique like PIXE, however the PIXE technique has another problem of integral nature in principle, therefore PIXE measurements are no longer surface sensitive. In any case, it is still interesting and useful enough to study the atomic structure by use of SP assuming the surface as an As-stabilized polar surface as widely accepted. The SP intensity can be directly evaluated if we compare the measured SP yields with the As yield in Fig.5(c).



Fig. 4 Increase of SP intensity calculated as a function of the lateral displacement distance of the first atoms in the Ga(001) string.



Fig. 5 Typical <001> aligned spectra for (a) c(4x4) and (b) (1x1) structures of GaAs(001) surface compared with (c) the random spectrum from a Si wafer with As implanted by 1.0x10¹⁶ cm⁻².



Fig. 6 Energy dependence of the <001> SP intensity for the c(4x4) (closed circles) and (lx1) (open circles) surfaces. Curves show the results of computer simulation which assumes (a) bulk-like structure and bulk-like surface thermal vibration, (b) bulk-like structure and enhanced (√2 times) surface thermal vibration and (c) bulk-like structue and doubled surface thermal vibration.

The energy dependence of the (001) SP intensity for both clean c(4x4) and hydrogen adsorbed (1x1) surfaces are shown in Fig.6 together with the results of computer simulation. In the simulation, we assumed the bulk termination for the surface structure with the bulklike thermal vibration (a) and enhanced surface thermal vibrations (b,c) which decay exponentially into the bulk value. It is obvious that the SP intensity from the c(4x4) structure is higher by \sim l atom/row even if we compare with the curve (c), while the SP intensity from the (lxl) surface is close to the curve (b) or (c). These provide firm evidence that the c(4x4) surface structure contains significant lateral displacements of at least 1 atom/row, i.e. 4 layers. In agreement with this, the non-normal <111> SP intensity for the c(4x4) surface, which is sensitive to both lateral and longitudinal

displacements of surface atoms, showed ~1.5 atoms/row increase as compared with the (lxl) surface. Further, the angular scan of the SP intensity for the c(4x4) surface around the $\langle 111 \rangle$ direction showed very symmetric but slightly broarder profile than the result of computer simulation which assumes again the bulk termination. This suggests that the longitudinal displacements of surface atoms, if any, are not uniform, in other words, some are expanded towards the vacuum and others are contracted.

The present results as described above apparently support a theoretical structure model by Ihm, et al²) however, more measurements are necessary to reach a definite conclusion.

Similar approach can be extended to interface studies in a straight forward manner. Figure 7 shows <001> alinged spectra from GaAs crystals covered by SiO_x layers. The SiO_x overlayer was made by plasma CVD keeping the GaAs The SiO_x layer substrate temperature at 250 °C. was then thinned by chemical etching. Provided the SiO_x overlyaer is sufficiently thin, the GaAs interface peak can be well revolved as in Fig.7(b). The Si and O peaks in this spectrum correspond to 1.8×10^{16} cm $^{-2}$ and 3.8×10^{-16} cm $^{-2},$ respectively, which is equivalent to $SiO_{2.1}$ layer of about 80 Å in thickness. On the other hand, the thickness of SiO_X layer in Fig.7 (a) is ~500 Å and in this case the interface peak does not appear due to the multiple scattering and struggling effects of the projectiles penetrating through the overlayer. The interface peak intensity in Fig.7(b), which comprises of the intrinsic scattering yield from the GaAs crystal and the scattering yield from any disordered interfacial layer, is slightly greater than that from the clean c(4x4) surface and represents that ~ 6 interfacial layers are out of registry. It is interesting to note that the thermally prepared SiO₂-Si interface is reported7) to is interesting contain only ≲l layer of such disordered atoms.

Another way to investigate the surface and interface atomic structure by high energy ion scattering is transmission channeling⁸), where we utilize high penetration power and the flux peaking effect of channeled MeV ions. The Si(111)-Pd system was studied with thin Si(111) crystals of $\sim 1 \ \mu m$ in thickness⁹). Figure 8 shows the scattering geometry and typical spectra obtained from the clean surface (open circles) and after Pd deposition of 0.9 ML coverage at



Fig. 7 Typical $\langle 001 \rangle$ aligned spectra from GaAs crystals covered by SiO_x layers. The overlayer thickness is (a) ~ 500 A and (b) ~ 80 A. The GaAs interface peak (IP) can be seen only in (b).



Fig. 8 Transmission channeling spectra from clean Si(111) surface (open circles) and after Pd deposition of 0.9 ML coverage The inset shows the scattering (dots). geometry where the scattering angle is ~85 degress.

The clean surface room temperature (dots). spectrum does not show any high energy feature at This corresponds to the about 400 channel. almost bulk-like structure of the clean Si(111) surface viewed in the normal direction¹⁰⁾. Deposition of Pd induces an appearance of the Si SP, which indicates Pd-induced distortion of the Si surface structure. Angular scans of Pd scattering intensities around the <111> direction gave a deep dip for 0.9 ML coverage and a flat profile for 12.4 ML coverage.

Although estimation of details of the Pd registry to the Si(111) surface structure is not available due to lack of precise information about the flux distribution of transmitted He+ ions and the lattice dynamics of the interface, there is no doubt that the Pd atoms in the initial stage have a tendency to be located on top of the Si(lll) strings. As we see in the marble model of the Si(111) surface in Fig.9, there are three different sites to fulfill the above requirement, on top of the first or second or fourth layer Si atoms. We cannot differentiate one of these from others, and also we cannot exclude possible penetration of the Pd atoms down to the subsurface sites of Si. However, some open sites such as marked by crosses in Fig.9 can be clearly excluded since these sites should show up a peak instead of the dip in the angular scan. The Si(111) SP intensity as a function of the Pd coverage showed that even the submonolayer coverage (\sim 0.4 ML) displaces \sim 1.7 ML of Si, however, beyond this initial stage, data plots lied between two lines representing the PdSi-and These results indicate Pd2Si-like relations. that Pd atoms deposit in the initial stage on registered sites accompanying large displacements of Si atoms, and then start formation of PdSi or Pd_2Si amorphous layer incorporating released Si atoms into the film.

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Fig. 9 Marble model of the Si(111) surface and possible sites for deposited Pd atoms. Arrows indicate possible directions of Si atomic displacements due to Pd deposition at the initial stage.

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