Coordination Determination of In on Si(100) from Synchrotron Photoemission Studies

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High-resolution core-level photoemission spectroscopy was used to study the initial growth and interaction of In on Si(100). The In-Si bonding coordination number, determined by quantification of the number of Si surface atoms selectively modified in the presence of an In adatom, is 3 for very low In coverages, and decreases to 2 for $\frac{1}{2}$-monolayer coverage. The results are consistent with a structural model deduced from electron diffraction, Auger, and scanning electron microscopy studies.

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We present a novel application of photoemission to a determination of the adatom-substrate bonding coordination number, a quantity of fundamental importance in surface studies. The system under study is Si(100) for various submonolayer In coverages deposited at temperatures of 50–100 °C. Changes observed in the Si $2p$ core-level line shape upon In deposition are identified as the selective modification of Si surface sites by the presence of In adatoms. The In-to-Si bonding coordination number is deduced from a quantification of the number of Si surface atoms modified in the presence of an In adatom. The variation observed in the coordination number for varying submonolayer coverages is shown to correlate well with a simple picture based on the consideration of chemical valence, and substantiates a structural model previously proposed on the basis of a study by low-energy electron diffraction (LEED), high-energy electron diffraction (HEED), Auger electron spectroscopy (AES), and scanning electron microscopy (SEM).[1]

The present experiment demonstrates an approach of general utility, and a significant implication is that surface properties and processes during adsorption and growth can be investigated and characterized to provide site-specific differentiation with a precision of much less than one atomic layer. Such capabilities could be of great value to the studies of Schottky barriers, heterojunctions, and, in general, epitaxial layers, which are topics of high current interest for fundamental reasons and their relevance to important industrial applications. Specifically, one serious obstacle to a detailed understanding of metal-semiconductor interfaces is that the geometric structure at the interface remains an unresolved issue in most cases. An accurate quantification of the adatom-substrate interaction is paramount to an

elucidation of the interface geometry. Furthermore, the Si(100) surface is technologically important. The In-Si(100) system represents a simple interfacial system involving elements of different nominal chemical valence. Recently, high-quality GaAs films have been grown on Si(100).[2] The present interest in the interface between group III-V and group IV semiconductors and the peculiar growth habit for these systems supplies the impetus for more fundamental studies such as the initial adsorption of group III materials on group IV substrates.

The photoemission experiments were carried out with synchrotron radiation from the University of Illinois beam line on the 1-GeV storage ring at the Synchrotron Radiation Center of the University of Wisconsin–Madison at Stoughton, Wisconsin. Light from the ring was dispersed by an extended-range grasshopper monochromator, which was designed and constructed by Hulbert *et al.*[3] A double-pass cylindrical-mirror analyzer was used to detect electrons emitted from the sample. The overall instrumental resolution was typically 0.2–0.3 eV. The n-type Si(100) samples were cleaned by thermal annealing at about 1100 °C for 10 sec. The surface was checked by HEED which revealed a sharp two-domain (2×1) pattern and occasionally a small mixture of (2×2). The In overlayers were prepared by evaporation with a rate of about 1 monolayer (ML) per minute. In this paper, 1 ML of In is defined as 6.8×10^{14} atoms/cm^2, which is the site-number density for an unreconstructed Si(100) surface. For each coverage, In was deposited upon a freshly cleaned Si(100)-(2×1) substrate at temperatures between 50 and 100 °C. In order to help differentiate the photoemission contribution of the Si surface atoms from that of the bulk crystal, two different photon energies, 140 and 108 eV, corresponding to surface- and bulk-sensitive conditions, respectively,

were used.[4-6]

A few typical surface-sensitive (140 eV) Si $2p$ core-level photoemission spectra are shown in Fig. 1 for various In coverages. Many other spectra for different coverages, and the bulk-sensitive spectra, are excluded from presentation because of space limitations. The spectrum for clean Si(100)-(2×1) shown in Fig. 1 shows an additional hump on the lower binding-energy side of the main spin-orbit–split peaks, which is indicative of a distinct surface core-level shift.[6] This hump is also present in the bulk-sensitive spectrum ($hv = 108$ eV, not shown) but with a much reduced relative intensity. By analyzing the bulk- and surface-sensitive spectra with a simultaneous least-squares fitting routine, we found that the spectra contained just one surface-shifted component in addition to the bulk component. The detailed analysis procedure will not be discussed here, but is very similar to the one previously reported for a similar system, Ge(100)-(2×1), and other related systems.[4,5,7] The deconvolution of the clean spectrum in Fig. 1 is indicated by the dashed curve for the bulk contribution (labeled B) and the dotted curve for the surface contribution (labeled S); the solid curve running through the data points is the overall fit, and the cubic background function is not shown. The abcissa in Fig. 1 (the relative binding
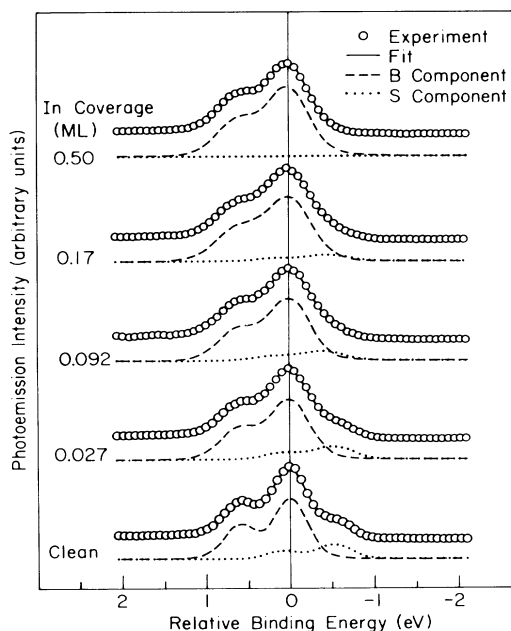

FIG. 1. Si $2p$ core-level spectra (circles) taken with a photon energy of 140 eV for clean Si(100)-(2×1) and In-covered Si(100). The coverages of In are indicated. The solid curves are the result of a fit to the data; the difference between the fit and the data is much smaller than the diameter of the circles. The decomposition of the spectra into the bulk (B) and surface (S) contributions is shown by the dashed and dotted curves, respectively.

energy) is referred to the bulk contribution of the Si $2p_{3/2}$ core. From the fit, the surface-induced core shift is 0.52 eV toward lower binding energies. The spin-orbit splitting, the branching ratio (intensity ratio between the $2p_{1/2}$ and $2p_{3/2}$ components), the Gaussian full width at half maximum (including instrumental broadening, phonon contribution, and inhomogeneous broadening), and the Lorentzian full width at half maximum (lifetime broadening) are 0.602 eV, 0.543, 0.18 eV, and 0.11 eV, respectively.

The surface- and bulk-sensitive Si $2p$ core-level line shapes for the In-covered Si(100) samples were analyzed in the same fashion; only some of the surface-sensitive spectra are shown in Fig. 1. Evidently, the distinct hump on the lower binding-energy side due to the surface-induced shift becomes smaller for increasing In coverages, and vanishes at about 0.5-ML In coverage and beyond. Thus, the Si surface atoms are affected by the In adatoms and converted to having a bulklike binding energy. The results of the fit are indicated in Fig. 1 by the solid, dashed, and dotted curves as in the case of clean Si(100)-(2×1) discussed above. In addition to the change in the intensity of the surface contribution, the only noticeable change in the line shape for increasing In coverages is a slight increase in the Gaussian width, most likely a result of inhomogeneous broadening and very small, unresolved shifts.

From the intensity ratio between the S and B components, R, the number of Si atoms contributing to the surface peak can be obtained from the following equation:

$$x = R \exp(d/\lambda)\{(1+R)[\exp(d/\lambda) - 1]\}^{-1}, \qquad (1)$$

where x is in fractions of monolayers, $d = 1.358$ Å is the interlayer spacing along the [100] direction of Si, and λ is the electron escape depth.[4,5] From previous studies of Si(111)-(7×7), we estimate the electron escape depth to be 4.9 ± 0.4 Å at 35 eV kinetic energy.[7,8] From our fit to the 140-eV spectrum for clean Si(100), we find $R = 0.25$. Using Eq. (1), we obtain $x = 0.83 \pm 0.05$.[6] A slight variation in x, about ± 0.02, was observed for the many clean samples that we prepared. A recent scanning tunneling microscopy study of Si(100)-(2×1) has revealed that the surface reconstruction is a consequence of the formation of dimers.[9] Both buckled and nonbuckled dimers are present in approximately equal numbers, while a small portion of the surface suffers from defects, most of which are related to missing dimers. An inspection of the large-area grey-scale topograph supplied in this study reveals that about 15% of the sample surface was covered with such defects. Our clean samples were prepared in a way similar to that used in the scanning tunneling microscopy work. Consequently, it is plausible that the observed Si $2p$ surface core-level shift is due to contributions from both buckled and nonbuckled dimers.

Since the two kinds of dimers are about equally energetically favorable, we expect the core-level shifts to be essentially the same for both kinds. That the surface-shifted component corresponds to less than unity monolayer may be attributed to the defects.

Using Eq. (1) and the measured values of R for In-covered Si(100), we have computed the average number of Si surface atoms which have been converted to having a bulklike binding energy for each In adatom. The result is shown in Fig. 2 as a function of In coverage. The uncertainty in the electron escape depth leads to an uncertainty of 7% in the data points. The random fluctuation of the data points is due to limited experimental precision.

Core-level shifts are only sensitive to the local bonding environment. Second-nearest–neighbor effects are much smaller. Since the energy shift of the surface Si atoms affected by the In is quite large (about 0.5 eV, on the order of the energy of a chemical bond), it is almost certainly the result of direct bonding between Si and In.[10] Thus, the data in Fig. 2 can be identified as the average In-to-Si coordination number for an In adatom on Si(100). The result indicates that the coordination number changes from 3 at very low coverages to 2 at about $\frac{1}{2}$-ML coverage. We will examine in the following whether or not these coordination numbers are consistent with the structure of the system.

The reconstruction phases of the In-deposited Si(100) surfaces depend on coverage and annealing temperature. A rather detailed surface phase diagram has been worked out, based on a combination of HEED, LEED, AES, and SEM studies.[1] For our samples of In on Si prepared between 50 and 100°C, the results can be summarized as follows: For coverages $\theta < 0.1$ ML, a two-dimensional "gas" is formed. For 0.1 ML$< \theta < 0.5$

ML, an In-induced (2×2) structure is present in addition to the Si(100)-(2×1). The (2×2) structure is fully developed at $\theta = 0.5$ ML. For 0.5 ML$< \theta < 1$ ML, the structure is a combination of the In(2×2) and another In(2×1) reconstruction. To account for all of the HEED, LEED, AES, and SEM results, about the only reasonable, and yet simple, structural model is as follows.[1] Figure 3(a) (from Ref. 1) shows a schematic drawing of the atomic structure of Si(100)-In(2×2), corresponding to 0.5-ML coverage. Notice that the Si dimers are still present; the In atoms simply form dimers with the dimer bond rotated by 90° with respect to the Si dimer bond and form rows parallel to the Si dimer rows. This structure saturates all Si dangling bonds while accounting for the valence of In. For 0.1 ML$< \theta < 0.5$ ML, some of the In rows are simply missing; while for 0.5 ML$< \theta < 1$ ML, the In in excess of 0.5 ML begin to fill in the (2×1) structure and form an epitaxial In(2×1) overlayer on the Si(100) surface. Based on this model, the In-to-Si coordination number at 0.5-ML coverage is 2, in agreement with the present result. Furthermore, the Si surface atoms bonded to In have a bulklike bonding configuration; therefore, their binding energies are expected to become bulklike,[10] in agreement with the experiment. For 0.5 ML$< \theta < 1$ ML, the line shape of the Si core level was observed to remain essentially the same as that for 0.5-ML coverage. The explanation is that the Si surface bonds are already saturated at 0.5-ML coverage; thus, further coverage of In does not lead to any significant changes in the Si bonding configuration. For low coverages ($\theta < 0.1$ ML), the In adatoms form a two-dimensional gas. The chemical valence of In is 3; thus, it is natural for an In adatom to bond to three Si surface atoms. This explains the experimental result that the initial In-to-Si bonding coordina-
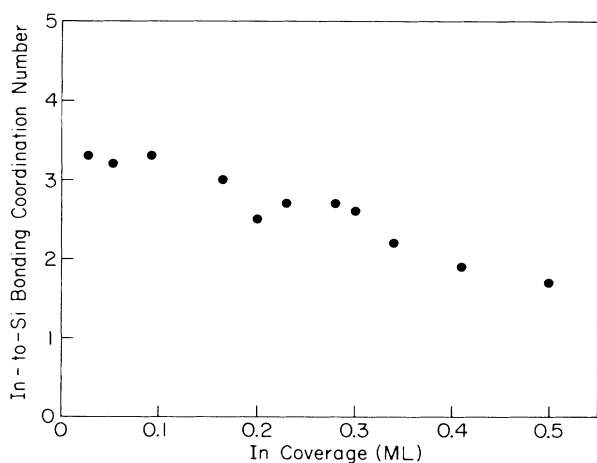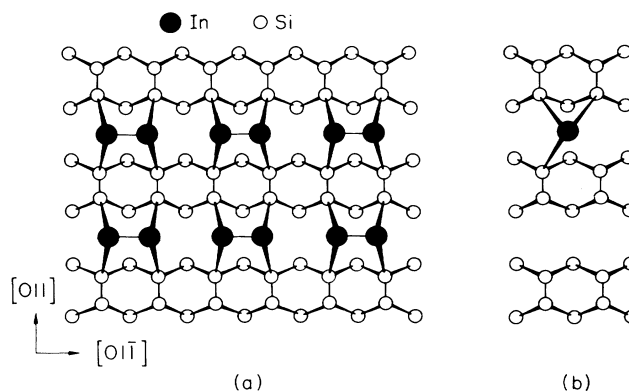

FIG. 2. The calculated average number of surface Si atoms affected by an In adatom (the In-to-Si bonding coordination number) for various In coverages.

FIG. 3. A picture of structural models for (a) the Si(100)-In(2×2) system (In coverage $\theta = 0.5$ ML) and (b) two-dimensional gas of In ($\theta < 0.1$ ML; only one In atom is shown). The In adatoms are shaded, while the Si surface atoms are not.

tion number is 3. The adsorption position of an isolated In adatom is likely to be similar to the ones indicated in Fig. 3(a) for dimers, except that the In dimer bond is replaced by an In-Si bond to the nearest Si surface atom, as schematically indicated in Fig. 3(b).

In summary, we have demonstrated a simple and straightforward approach for determining the adsorbate-substrate coordination number for a simple system, In on Si(100). By analyzing the Si $2p$ core-level spectra, we have identified the selective modification of certain surface sites in a framework which seeks to quantify the In adatom-substrate interaction and discern rudimentary features underlying the growth mechanism. By determination of the bonding coordination number for any semiconductor-metal overlayer system, structural models and adsorption interaction theories can be further scrutinized.

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