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Arsenic atom location on passivated silicon (111) surfaces

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The position of As atoms on a clean Si(111) surface has been determined with x-ray standing waves in ultrahigh vacuum. The As atoms occupy exclusively the top half of the silicon (111) double plane and lie at 0.17 Å above the unrelaxed bulk terminated silicon (111) plane. This value is in good agreement with recent total-energy minimization calculations. A significant but limited stability of As passivated surfaces is observed upon exposure to various ambients. We also present general arguments showing how surface specificity can be achieved with x-ray standing-wave measurements such as the above, where bulk-symmetry site-occupancy rules are broken.

One of the more challenging problems in surface physics or chemistry lies in the preparation of passivated nonreactive surfaces. Over the years many attempts have been made to prepare such surfaces both by wet chemical methods[1,2] and under more controlled ultrahigh-vacuum (UHV) environments.[3,4] Since a passive layer usually involves about a monolayer of impurities, the problem of the location of atoms in this layer poses some difficulties. Usually one has had to rely on indirect methods to infer the location of the passivating species. More recently, powerful new x-ray techniques have been sufficiently developed to begin to address such problems. Some years ago Cowan, Golovchenko, and Robins[2] demonstrated that the x-ray standing-wave method could be used for the location of Br atoms adsorbed by wet-chemical methods on the (110) surface of silicon. Since Br with one extra electron can satisfy a dangling bond at the (111) surface of silicon, a Br-covered (111) surface could provide an ideal termination of the silicon (111) plane. It was difficult in these experiments to obtain surface Br coverages greater than 0.1–0.2 ML (1 ML $= 7.8 \times 10^{14}$ atoms/cm^3) on the (111) surface of silicon. Thus 80%–90% of the surface was characterized in the Br work. In a much more controlled well-characterized experiment Bringans and co-workers[4,5] have succeeded in passivating Ge and Si (111) surfaces with As under UHV conditions. These authors hypothesize that As is an ideal termination for bulklike (111) surfaces with As atoms substituting for silicon atoms at the topmost site of the silicon (111) double plane. The validity of this hypothesis has been tested using angle-resolved photoemission on As terminated Ge and Si surfaces and pseudopotential calculations of such surfaces. The latter method deals directly with the electronic properties at the surface from which atomic scale geometrical information is inferred. In the following, we shall show that the location of the As atoms at the surface can be directly terminated with atomic positions established accurately enough to test the most sophisticated calculational methods currently available. Under ideal conditions the positions of the atoms can be measured to 1% of the relevant d spacing.

The x-ray standing-wave method has been described in previous publications.[6] Very briefly during strong Bragg reflection from a highly perfect crystal, the coupling between the incident and diffracted beams gives rise to a standing-wave field that extends outside the surface of the diffracting crystal and has the periodicity of the Miller planes responsible for the reflection. As the crystal is tilted through the region of total reflection the standing waves move continuously by half the planar spacing along the operative reciprocal-lattice vector. If the impurity fluorescent scattering from the standing-wave field is monitored, a maximum is observed when the standing-wave antinodal plane passes through the impurity position. Conversely, a minimum in the impurity fluorescence is observed when the nodal plane passes through the impurity position. Since the x-ray dynamical theory predicts the phase of the standing-wave field with respect to the crystal lattice planes, as one tilts through the total reflection region the position of the impurity with respect to the lattice can be simply deduced.

An important consideration in applying x-ray standing-wave methods to problems of atom location in surface physics concerns the inherent lack of surface specificity of fluorescent or other secondary signals used to detect impurities. One must typically be assured by alternative surface techniques that all impurities being studied are at the crystal boundary rather than in the bulk. In the case studied here such concerns are completely alleviated by recognizing the following general symmetry argument. Atomic locations occupied by impurities in the bulk crystal may generally be assumed on average to satisfy the symmetry group of the crystal. Thus, for example, atomic positions of impurities *in* a centrosymmetric crystal should yield average impurity positions with this same symmetry. For atoms *on* the surface, this symmetry is broken and average measured impurity positions need not satisfy the above constraints. More interestingly, if experimental measurements show that such unsymmetrical results are obtained one is generally assured that the atoms are in a nonsymmetrical environment such as the crystal surface. The results we present below show exactly this behavior and no further demonstration that all the impurity atoms are at the surface is necessary.

Substrates for the UHV experiments were prepared by Syton polishing an accurately oriented (111) crystal of silicon. The polished surface was chemically cleaned following the procedure outlined by Ishizaka, Nakagawa, and Shiraki[7] (Shiraki etch). After cleaning, heating at a moderate temperature, $\sim 850\,^{\circ}$C in a UHV environment

(base pressure 8×10^{-11} Torr), was sufficient to produce a sharp (7×7) LEED (low-energy electron diffraction) pattern. The substrate was then positioned opposite an outgassed and precleaned As effusion cell operated at $\sim 280\,^{\circ}$C. With the specimen held at $800\,^{\circ}$C the As shutter was opened and the sample cooled in the As beam in 2.5 min to $400\,^{\circ}$C; at this temperature the specimen was further exposed to the beam for 2.5 min. The As shutter was then closed and the sample and the furnace cooled to room temperature. This procedure is similar to that used by Olmstead and co-workers[5] and was essential to obtain coverages in the monolayer range. A sharp (1×1) LEED pattern was observed after As deposition. The Auger spectrum showed no detectable oxygen and a trace amount of carbon. The As coverage was determined by RBS (Rutherford backscattering). The maximum coverage obtainable using the specimen preparation described above was ~ 0.93 ML.

The reflectivity and As fluorescence yield for a crystal prepared as described above is shown in Fig. 1. The experimental points together with the error bar are shown in the figure. The solid line represents the theoretical fit to the data calculated from x-ray dynamical theory. Both the position $\mathcal{P}$ and coherent fraction $\mathcal{F}$ (designated as POS and FRAC, respectively, in a previously published article) are shown, with $\mathcal{F}$ being defined as the fraction of atoms at the value of $\mathcal{P}$ indicated. For an unrelaxed bulk terminated upper half of the silicon (111) double plane, $\mathcal{P} = 1.125$ and $\mathcal{F} = 1$. The experimentally determined value for the As position in Fig. 1 is $\mathcal{P} = 1.18$ and $\mathcal{F} = 0.98$. The absence of a signal associated with As atoms at additional sites near plane (b), which is consistent with the symmetry of the bulk, is a manifestation of the general argument previously given that here we are only observing signals from atoms at the surface.

One can obtain a physical feeling for the strong maximum observed in the As fluorescence signal with the aid of the inset in Fig. 1, which shows a [110] projection of the silicon (111) double planes. Dynamical diffraction theory predicts the phase of the standing-wave field relative to that of the electron density Fourier component responsible for the diffraction. In this case, the (111) Fourier component has its maximum between the close spaced (111) atomic planes. As the crystal is tilted to high Bragg angle, the nodes of the standing-wave field move along the inward drawn normal to the crystal surface. Thus, if the atoms were situated on plane (b) the fluorescence would show a large dip in the Bragg gap region. However, it is the antinodes that will pass through plane (a); therefore, a large peak will be observed in the fluorescence yield, which is the situation that is observed in Fig. 1 for As covered silicon. From the $\mathcal{P}$ values indicated the As atoms lie about 5% of the (111) d spacing above the position for perfectly terminated bulk silicon.

It is important to note that it is possible to obtain results that differ from the above using varying deposition conditions. In Fig. 2 we show the influence of varying substrate temperature on the fluorescence yield. The three variables $\mathcal{P}$, $\mathcal{F}$, and coverage appear to be a strong function of substrate temperature. At the lowest temperature, $350\,^{\circ}$C, a monolayer of coverage is obtained, however, $\mathcal{P}$ is now 1.0, and the coherent fraction is only 0.41. At $500\,^{\circ}$C the coverage decreases to 0.7 ML but the coherent fraction improves to 0.57 while $\mathcal{P} = 1.15$. Finally at $600\,^{\circ}$C the total coverage obtainable is only 0.5 ML but now $\mathcal{P} = 1.17$ and $\mathcal{F} = 0.73$. The last $\mathcal{P}$ is close to the value observed in Fig. 1 for the specimen cooled in the As beam from $800\,^{\circ}$C. During the course of these experiments the visually observed (1×1) LEED did not change, which further emphasizes the unique structural sensitivity of the x-ray standing-wave method.

In their angle-resolved photoemission studies, Bringans and co-workers[4,5] have emphasized the remarkable chemical passivity of the As stabilized Si or Ge surface. In Fig. 3 we show some standing-wave results upon exposure of the As covered surfaces to various environments. For the topmost curve in Fig. 3 exposure to 10^5–10^6 L O_2 did not change the original $\mathcal{P}$ or $\mathcal{F}$ value even for a 0.5 ML As covered surface. However, an exposure of 10^5-L atomic H (where 1 L $= 10^{-6}$ Torr sec) contracts the As layer to the bulklike terminated Si position and also reduces the coherent fraction. Finally, after exposing the specimen
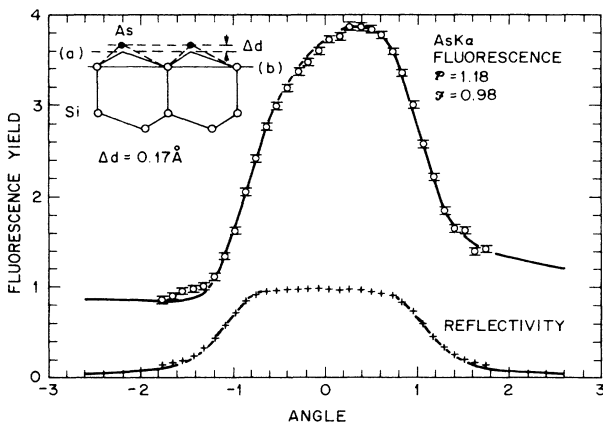

FIG. 1. Reflectivity and fluorescence yield for As on silicon deposited according to procedure outlined in text, As coverage 0.93 ML, shown on a reduced angular scale. Full width at half maximum of the reflectivity curve $\simeq 3$ sec of arc.
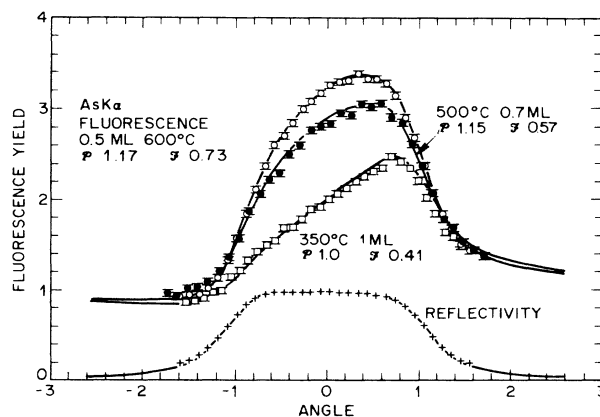

FIG. 2. Reflectivity and fluorescence yield for As on silicon deposited at fixed substrate temperature.
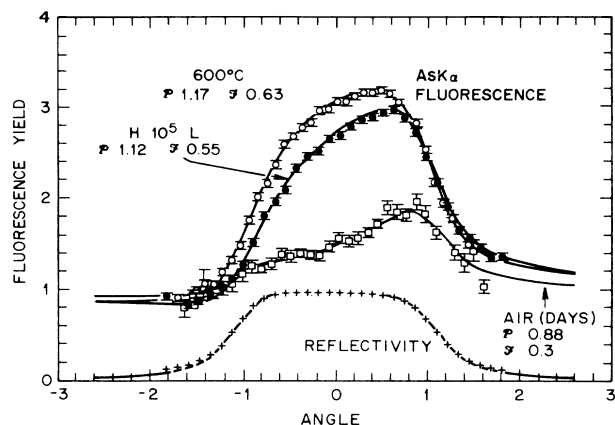
FIG. 3. Reflectivity and fluorescence yield for As on silicon, influence of various ambients.

shown in Fig. 1 to air for one day, we note that the surface is almost completely disordered with about 30% of the atoms at a position close to the lower half of the (111) plane, the rest being in random positions.

We compare now our findings in Fig. 1 with recent first-principles pseudopotential total-energy minimization calculations of the As terminated surface. Such sophisticated calculations are possible in cases where the unit cell of the surface structure is simple such as the (1×1) case. Assuming that this is the case as borne out by LEED observations, Northrup[8] has calculated the As position on an As terminated silicon surface. His value of 0.19 Å for Δd (see inset in Fig. 1) can be compared to our experimental x-ray standing-wave result of $\Delta d = 0.17 \pm 0.03$ Å. All displacements are indicated in Å from the bulk terminated

silicon positions. In a more recent calculation, Hybertsen and Louie[9] find a value of 0.16 Å for Δd. Our experimental value of 0.17 Å lies between the theoretical estimates. Both theoretical results are well within experimental uncertainty and agree with each other within the expected precision of these calculations for surface geometry.

Copel and Tromp[10] have suggested from RBS measurements that the saturation coverage of 0.93 ML As may be explained if half the surface is faulted, suggesting that the As termination has not eliminated the faulted region on the original (7×7) surface. In support of this hypothesis these authors also report a coverage of ~0.9 ML as the limiting coverage, an observation which is borne out by our measurements and further in situ measurements by RBS.[11] On the other hand, there has been no evidence of any residual 7×7 features on these As terminated surfaces by LEED. The presence of stacking faults on the surface can be directly resolved by off-normal x-ray standing-wave measurements[12] involving the 220 Fourier component of the charge density. Since this involves major modification of our UHV apparatus we defer this experiment for the future.

In summary, As atom positions on a silicon (111) surface have been accurately determined using x-ray standing waves. With an extremely high degree of coherence As atoms occupy exclusively the top of half of the (111) double plane expanded outward by ~5% from the bulk terminated silicon lattice. Significantly the As positions as calculated from first-principles total-energy minimization calculations, are in excellent agreement with the value found from the standing-wave measurements.

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