In-situ Spectroscopic Study of the As and Te on the Si (112) Surface for High-quality Epitaxial Layers

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A detailed analysis of the As-exposed Si (112) and subsequent Te exposure was performed. X-ray photoelectron spectroscopy shows that the Te- and As-exposed Si (112) surface had 70% As and 27% Te coverage, respectively. Direct surface coverage measurement with ion scattering spectroscopy (ISS) shows that the Si (111) surface is completely covered by As, and that of the Si (112) had about 78% and 20% coverage of As and Te, respectively. Finally, using ISS shadowing effects, it was found that the Te atoms were positioned mainly on the step edges.

Key words: Te/As/Si (112), adsorption, molecular beam epitaxy (MBE) substrate, x-ray photoelectron spectroscopy (XPS), ion scattering spectroscopy (ISS)

INTRODUCTION

High index Si surfaces are used in the fabrication of HgCdTe third generation thermal imaging and electronic systems;[1–4] however, there is a substantial lattice mismatch with the MBE-deposited epitaxial overlayers. However, high-quality B-face CdTe and subsequent HgCdTe epilayers can be achieved when the Si surface is passivated with As because it allows the Te to find the optimum nucleation site for growth on the nonpolar Si surface.[5] The Si (112) surface is the current principal substrate for epitaxial growth of polar semiconductors on Si. While the Si (112) surface has such possibilities, limited knowledge is available about its atomic structure, orientation stability, and precursor treatments. An understanding of the early stages of heteroepitaxial growth on the Si (112) surface will enable optimized growth of high-quality epitaxial layers. With experimental and theoretical calculations, several studies have addressed the problem of As coverage and have suggested the location of these atoms is on the Si (112) surface.[1,6–8] However, no direct measurement of the locations of Te and As on the Si (112) surface has been reported.

Numerous approaches have been undertaken to improve the quality of the CdTe layer.[9–11] The most common approach used for the Si (112) surface is the formation of a thin buffer layer of ZnTe after As and Te exposure, followed by the formation of CdTe and subsequent HgCdTe growth. The bulk terminated Si (112) orientation consists of (111) terraces and (100) "risers" oriented 19.5° and 35.3° off the surface normal, respectively. This stepped surface allows a step flow (Frank-vander Merwe) growth mechanism that leads to minimum twinning and antiphase domain formation. At elevated temperatures, the Si (112) surface reconstructs into quasiperiodic, nanometer-scale facets.[12] However, As passivation of the Si (112) surface reverts back to a longer terrace-multiple step structure.[7]

In this study, we present experimental evidence of the outermost Si (112) surface with a standard As layer and subsequent Te deposition to clarify and support existing information. A standard technique, based on Scofield photo-ionization cross-sections, mean free path and number of surface atoms, was used to obtain As and Te coverage with x-ray photoelectron spectroscopy (XPS). We developed a process to obtain direct surface coverage with ion scattering spectroscopy (ISS). Finally, we used the surface sensitivity and shadowing effects of ISS to find the locations of the As an Te atoms on the Si (112) surface.

EXPERIMENTAL

The Si (112) surface was hydrogen passivated ex situ using a recipe[13] that has proven to give excellent inert characteristics. Upon loading the substrate into the MBE chamber, the H was desorbed

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by ramping to 700°C while also exposing the surface to an As_4 flux. In the standard procedure, cooling to ~300°C is expected to produce an As monolayer on the Si (112) surface. To further ensure monolayer coverage for this work, the substrate was first cooled to room temperature under an As_4 flux (~2×10^{-6}) to produce a thicker As film. The substrate was then heated to 500°C to remove the thicker film, leaving only a single layer of chemisorbed As atoms. This procedure was closely monitored by observing the reflection-high energy electron diffraction (RHEED) pattern, which is completely featureless for amorphous As but indicates a 2×4 reconstruction for the chemisorbed monolayer. The thick As films were obtained via exposure to an As_4 flux for ~2 hr at room temperature. In other experiments, Si (112) surfaces passivated with an As monolayer were also subjected to a Te flux (~1×10^{-7}) for 25 sec. The latter procedure established a surface that has been used for subsequent ZnTe migration enhanced epitaxy and CdTe growth. Transfer to the surface analysis chamber was carried out in vacuo. XPS data were obtained at a base pressure of 5×10^{-10} torr with either Mg K_α at 1253.6eV or monochromatized Al $K_{\alpha(1,2)}$ x-rays with energy of 1486.6 eV, a pass energy of 2.95 eV, and at a take-off angle of 45° to minimize diffraction effects. All binding energies were corrected for charge shifting by referencing to the adventitious carbon (C1s) line at 284.6 eV. ISS measurements were performed at a He base pressure of 3×10^{-9}, using 1 keV $^3He^+$ ions (enhances energy resolution for light elements) with a landing current of 10 nA. The ion gun and analyzer were positioned at a scattering angle of 134° to avoid most of the background signals originating from neutrals, re-ionized ions, and most secondary events.

RESULTS AND DISCUSSION

Passivation of the Si (112) Surface

The Si (112) surface is passivated with a HF-containing solution generating a stable H-terminated surface. An ISS spectrum of a Si (112) surface is given in Fig. 1a. The spectrum consists of peaks at about 0.581, and 0.694 and an intense yield at low energies. The peaks are characteristic of scattering from F and Si, respectively. The intense yield at low energies is interpreted as caused by sputtered H^+ ions that originate in a high concentration of H atoms at the surface. Note the absence of peaks due to either C or O, as they were observed in amounts smaller than F in XPS spectra. This could be due to low concentration beneath the H overlayer or to their high sputtering efficiencies. Figure 1b depicts the XPS spectra of the Si2p, F1s, and wide scan from the H-terminated Si (112) surface. No Si–F, Si–O, or Si–C bonding is observed, and there is less than 2% C and O and less than 4% F on this surface. More details for our cleaning process can be found elsewhere.[14] The H and F and other species are desorbed by ramping the temperature to about 700°C, leaving a clean Si (112) surface for subsequent As and Te exposure.

As and Te Coverage

The As passivated Si (112) surface is thought to provide a balance of charges at the interface and electronically match the Si surface to the II-VI compound. This As passivated surface allows Te to find the optimal site for nucleation of B-face growth. As mentioned earlier, work has been done to assess the As and Te coverage of the Si (112) surface using XPS and Auger electron spectroscopy (AES). The AES results yielded a coverage with As, accounting for

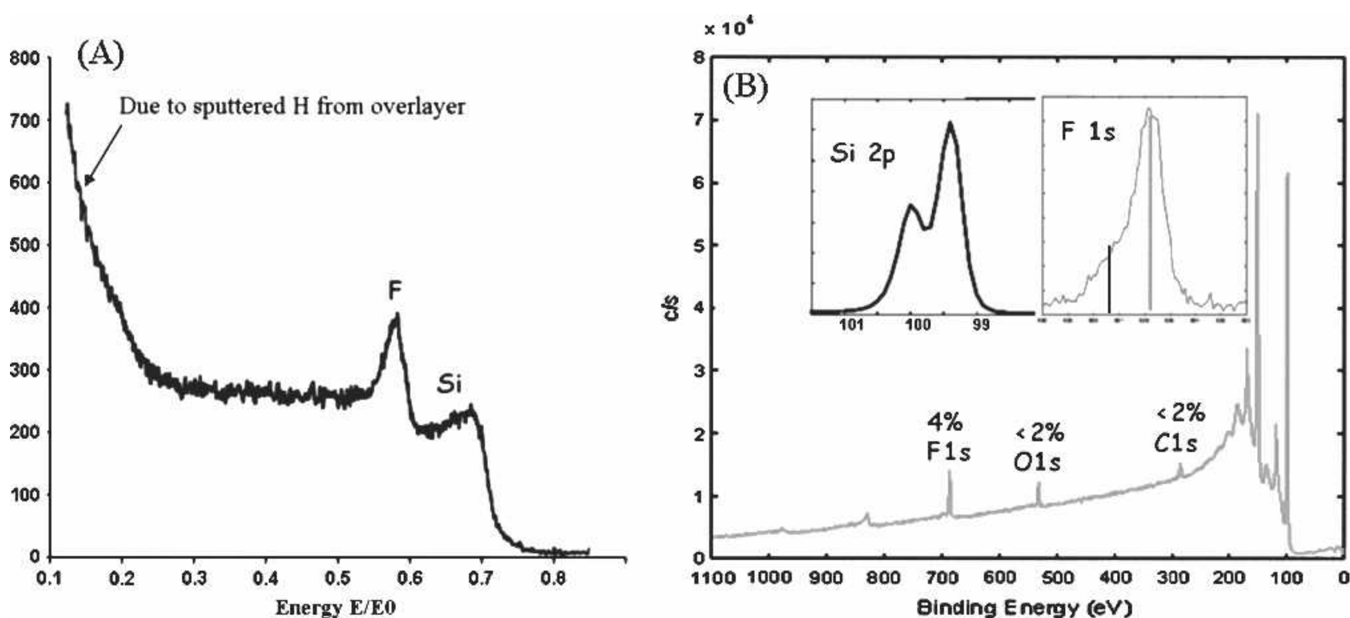

Fig. 1. (a) ISS of a H-terminated surface, showing the starting surface before As passivation. (b) XPS spectrum of Si2p, F1s, and wide scan. The passive film consists of H, adsorbed O, C, and F on the outer surface.

about 2/3 (As) and (1/3) Te of a monolayer.[1] Subsequent studies have addressed the problem with experimental and theoretical calculations, yielding either 2/3[6,7] or 3/4 As (1/4 Te)[8] coverage on the Si (112) surface. Figure 2a shows a survey XPS spectrum of the Si (112) surface after our standard As and Te exposure. The spectrum shows no O or C contamination species present. Figure 2b illustrates XPS spectra for the Si2p, As3d, and Te3d lines after our standard As and Te deposition. To set a benchmark, we have used the method reported by Fulk et al.[6] for calculating the As and Te coverage for our process. The standard method is based on Scofield photoionization cross-sections, mean free path, attenuation factors, and geometry/number of surface atoms. For our process, the As and Te covered about 70% and 27% of the surface, respectively. These results are in agreement with those found by several studies using the same procedure,[6–8] and those by the first reported results using AES.[1]

Because of the high neutralization probabilities and scattering cross sections of low energy ions, ISS enables the selective analysis of the outermost atomic layer.[15] The elastic binary collisions of $^3He^+$ ions provide an energy spectrum that is characteristic of the distribution of the masses that originate exclusively from the surface monolayer atoms. Thus, using ion neutralization effects, ISS can provide a direct measurement of the As coverage. To understand the details of the adsorbed layer on the Si (112) substrate, we calibrated the data using a bulk As sample. Figure 3 illustrates the ISS spectra from a thick As layer (solid line) and from the Si (112) surface after the formation of an As monolayer (dotted line) during our standard method. The solid line shows only one peak at 0.872 corresponding to As, and the dotted line shows an additional peak at 0.694 due to Si. Comparison of the ISS of a bulk As sample and the standard precursor As monolayer

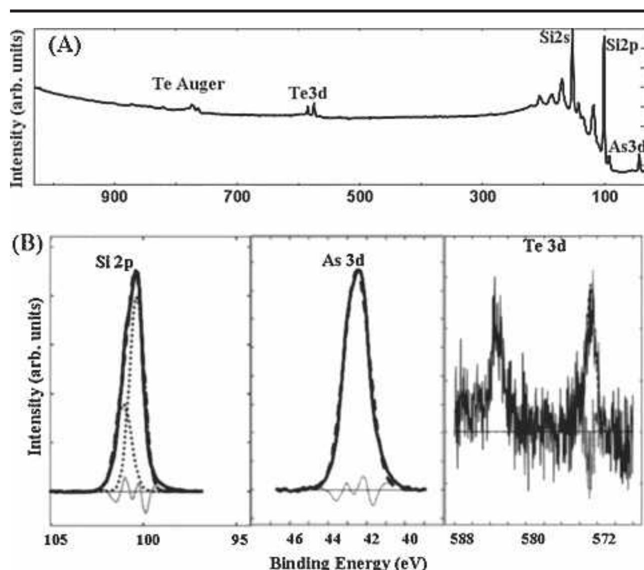

Fig. 2. MgKα XPS spectra of the As and Te exposed Si (112) surface (a) survey spectrum showing all the elements present and (b) narrow scan regions for the Si2p, As3d, and Te3d lines.

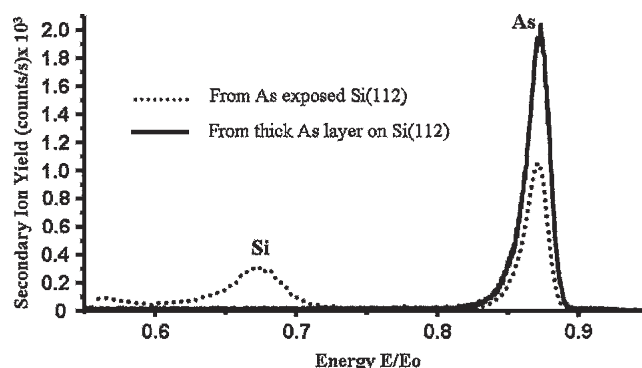

Fig. 3. The solid line is an ISS of a thick epilayer deposited by MBE, depicting the signal obtain from a bulk As sample. The dotted line is of a As monolayer deposited on the Si (211) surface. The data suggest that a normal As passivation step leaves unbonded Si on the surface.

indicates that about 40% of the Si surface atoms are unoccupied. The As coverage found by this procedure is lower that those obtained by XPS. The lower coverage found might be due to contributions to the backscattered yield from atoms in the second layer of the thick As film. As a result, an alternative calibration procedure is needed. This could be resolved by using the Si (111) surface, which is know to form a nearly complete monolayer of As on its surface.

Figure 4a shows ISS spectra from an As monolayer formed on the Si (111) surface obtained at take-off angles of 45° and 28°—solid and dotted lines, respectively. The solid line from the take-off angle of 45° denotes similar characteristics of a typical As monolayer on a Si (112) substrate. However, the dotted line spectrum (at 28°), shows no Si peak at 0.694. Several extensive studies have shown that upon As adsorption on the Si (111) surface, As adatoms occupy the top sublattice sites of the (111) bilayer, as shown in Fig. 4b.[16–20]

We have used ISS shadowing effects to asses the monolayer coverage of the Si (111) surface. If a beam of ions is incident or backscattered along a major crystallographic axis, the closer the incoming ion is to the first scattering atom, the larger the deflection will be. The outcome is that a shadow cone is formed behind the first scattering atom. The radius of the shadow cone depends on the atomic numbers of the projectile and target atoms, and it decreases roughly with the square root of the energy. Therefore, low energies correspond to wide shadow cones. The choice of the shallow angle (28°) and azimuthal direction [(112) planes facing the analyzer], was based on the geometry reported in the literature and is shown in Fig. 4b.[16–20] At this angle, the As atoms will shadow nearly all the backscattered $^3He^+$ from the Si atoms in the second layer, diminishing the collected ions of the Si peak at 0.694 as shown in the dotted line in Fig. 4a. Our results are evidence of full As monolayer coverage based on the geometry of Fig. 4b, in which the top Si atoms of a bulk terminated Si (111) surface are replaced by As atoms. Figure 4c summarized our results, showing a model of the resulting stable, As–Si (111) surface.

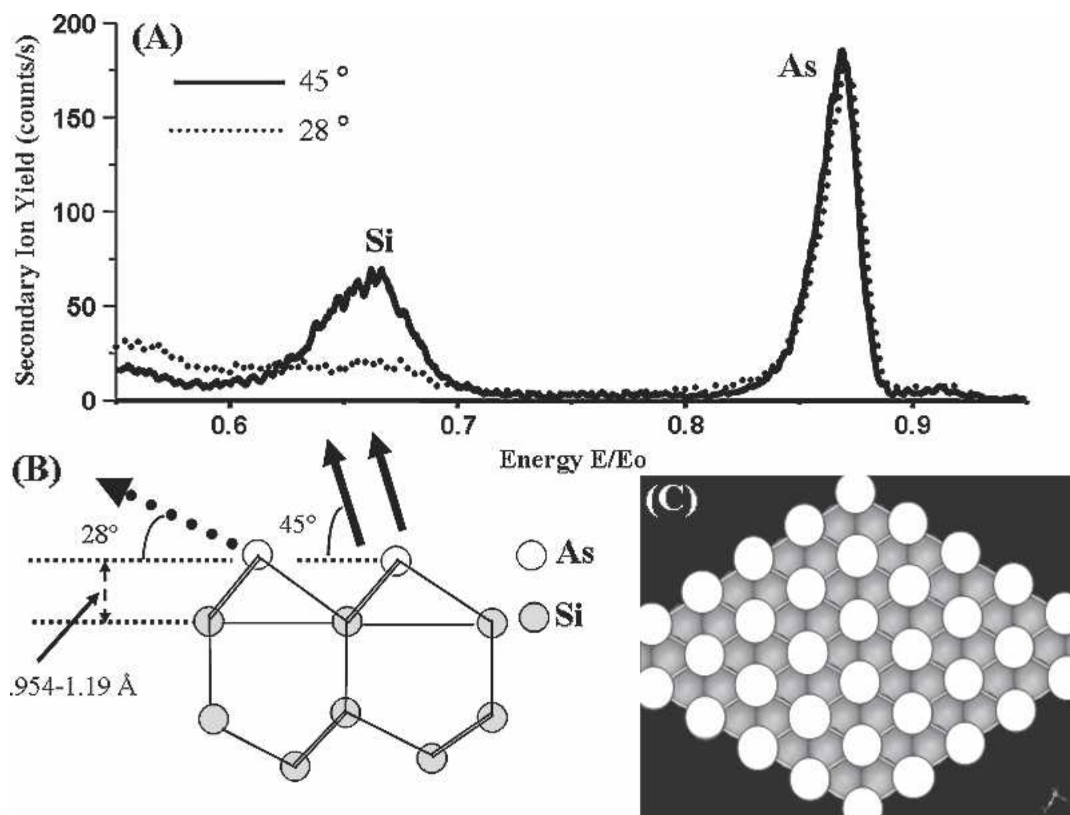

Fig. 4. (a) ISS from an As monolayer on the Si (111) surface at a take-off angles of 28° and 45°, (b) Side view in the ($\bar{1}$10) plane of the Si (111) surface, (c) model of the resulting stable As–Si (111) surface.

We used the ISS data from the Si (111) surface as the calibration for one monolayer of As on the Si substrate. The solid line in Fig. 5 shows ISS spectra of an As monolayer on Si (111), and dotted and dashed lines represent ISS data from an As monolayer and the standard As and Te deposition on the Si (112) surface, respectively. Assuming the total effective number of atoms that contribute to backscattering yield comes from the same surface region, the comparison of their respective intensities to the reference spectra [ISS from As monolayer on Si (111)], the fraction coverage can be determined.

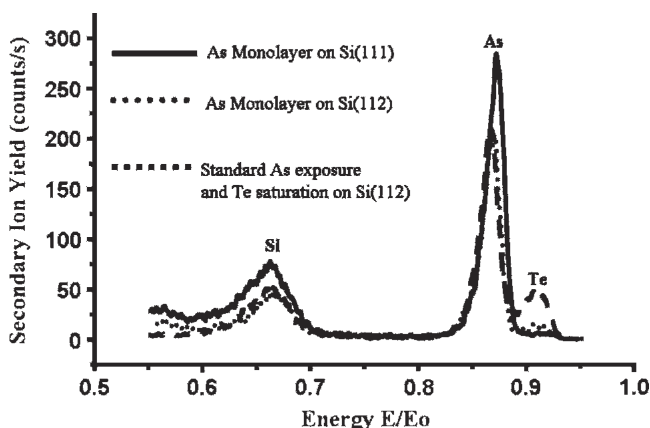

Fig. 5. ISS spectra of an As monolayer on the Si (111) surface (solid line), As monolayer on the Si (112) surface (dotted line), and As and Te deposition on the Si (112) surface (dashed line).

We obtain an As surface coverage of about 78% for both the As monolayer and the standard As and Te deposition on the Si (112) surface. This value is within those reported for As exposure and slightly higher for the As and Te exposure. Nevertheless, our results come from a direct measurement of the top atoms and a well-calibrated reference. On the other hand, Te is found to have a 20% coverage on the Si (112) surface, which is lower than those reported in previous studies. This lower value in Te coverage could be due to different scattering cross-section factors in ISS because we used the intensity of the As peak from the Si (111) as a reference.

Location of As and Te

Previous work has suggested that As and Te chemisorption occurs preferentially at terraces and step edges; however, these results were reported based on the relative areas of the terraces to steps. No direct experimental evidence of the location of these atoms has been reported previously. We have outlined the inherent capabilities of ISS in assessing the top atoms on a surface. Here, we used the intrinsic monolayer sensitivity and shadowing effects of ISS to find the position of the Te and As atoms. Figure 6a shows the resulting ISS spectrum when either the steps or terraces are facing the analyzer—solid and doted lines, respectively. The orientation of the (111) terraces were located using photoelectron diffraction in XPS and the flat of the

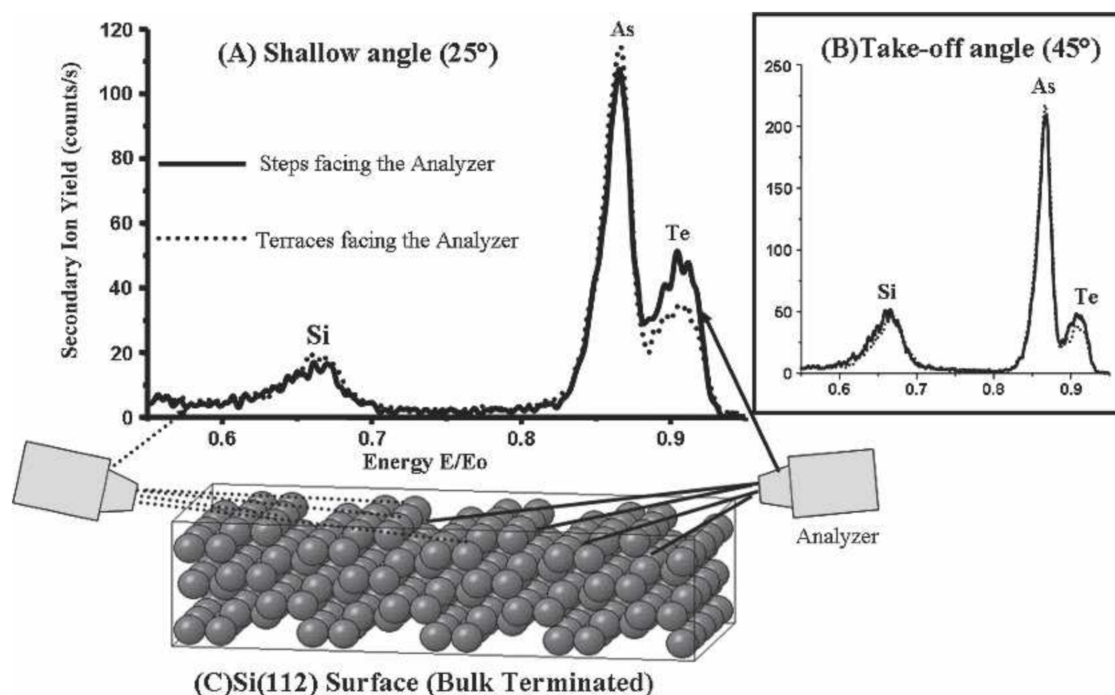

Fig. 6. (a) ISS spectra of a shallow angle (25°) when the steps are facing the analyzer (solid line) and terraces facing the analyzer (dotted line). (b) Same as in (a) but at a take-off angle of 45°. (c) Model of the bulk terminated Si (112) surface.

Si (112) wafer. An increase in the photoelectron intensity happens when the normal to (111) terraces are facing the analyzer at a take-off angle of 70.5°. Then the steps could be positioned to face the analyzer by rotating an azimuth angle of 180°. To increase the surface sensitivity, the sample was positioned at a shallow take-off angle of 25°, as shown in the illustration in Fig. 6c. The increase in the secondary ion yield for Te; at 0.923, in the solid line in Fig. 6a is taken as evidence that the Te atoms are positioned in the step edges. In addition, when the terraces are facing the analyzer, a slight increase is observed at 0.872 for As atoms. Figure 6b represents a take-off angle 45°, showing the same trend but less noticeably. Nevertheless, it provides further evidence that the Te atoms are positioned on the step edges and the As atoms on the terraces. These are important results because they provides, for the first time, experimental confirmation of such a claim. Moreover, such results have implications for optimizing the growth to produce high-quality epitaxial layers on the Si (112) substrate.

CONCLUSIONS

In summary, we have performed a detailed study of the As and Te deposition on the Si (112) surface. XPS showed 70% and 27% of As and Te coverage, respectively. ISS provides direct measurement of the surface coverage. ISS measurements show that a complete As monolayer is formed on the Si (111) surface. Using this reference, ISS shows that the Si (112) surface has about 78% and 20% coverage of As and Te, respectively. Finally, we have shown experimentally that the Te atoms are positioned mainly on the step edges and As on the terraces.

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