

## Au/H:Si(111)-(1×1) interface versus Au/Si(111)-(7×7)

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The room-temperature growth of gold on Si(111) surfaces has been directly compared for nonreconstructed hydrogen-terminated surfaces and the bare 7×7-reconstructed surface by means of high-resolution core-level and valence-band photoelectron spectroscopy and Auger spectroscopy. The growth modes show strong differences with gold island formation on the passivated H:Si(111)-(1×1) surface. Silicon segregated on top of the deposited gold film is seen for both interfaces. The Schottky barrier is only weakly affected by the hydrogen termination. [S0163-1829(98)01508-2]

### I. INTRODUCTION

Hydrogenation of silicon surfaces by *ex situ* wet chemical processing yielding high-quality nonreconstructed surfaces has led to numerous studies of this model surface. The simple structure of this surface allows comparisons to calculations for nonreconstructed surfaces.<sup>1</sup> The high degree of order and passivation makes it an ideal starting point for the analysis of model interface formation. Surface passivation is known to influence the growth mode of adsorbates and can lead to modified interface structures. Whether macroscopic electronic properties (e.g., Schottky barrier height) are governed by the bulk properties of substrate and adsorbate or entirely determined by the interface structure has been a controversial issue ever since interfaces are studied. Much of the controversy arises from different preparation methods yielding different interface quality. By now surface science techniques give better control of sample preparation. Modification of the interface structure by an intercalated passivating layer in combination with comparative studies should shed new light on the subject. Interfaces formed with silver,<sup>2-4</sup> aluminium,<sup>5,6</sup> cobalt,<sup>7</sup> nickel,<sup>8</sup> copper,<sup>9</sup> and lead<sup>10</sup> have been studied as well as the influence of hydrogen termination on the growth of metal phthalocyanides,<sup>11</sup> indium phosphite,<sup>12</sup> and silicon<sup>13</sup> on silicon surfaces. In many cases the hydrogen termination induces island growth<sup>5,7,8,3</sup> or promotes the growth of epitaxial films<sup>2,13,4,12</sup> compared to the bare silicon surface. The intercalated hydrogen layer is partially removed by the growth.<sup>2,7,3,8</sup> The aim of this letter is to present the influence of hydrogen passivation on the properties of a reactive interface like Au/Si(111). In order to improve the reliability of the different techniques used for sample preparation and spectroscopy, a direct comparative study of bare and hydrogen-terminated surfaces is chosen. This approach is necessary if the differences between the studied systems are small and possibly related to the preparation (e.g., different adsorbate coverages).

### II. EXPERIMENT

The experiments were carried out at the SuperACO (LURE) 800 MeV synchrotron on high-resolution beamline SU3 equipped with a PGM-monochromator upgraded to spherical mirror optics. Overall energy resolution is better

than 40 meV over the whole energy range. The angular acceptance of the analyzer is less than 2°. Samples are cleaned by chemical growth of a thin oxide film<sup>14</sup> which is desorbed *in situ* at 850 °C yielding a sharp 7×7 reconstruction as checked by low-energy electron diffraction (LEED). This low-temperature preparation results in contamination-free well-ordered surfaces and avoids dopant surface segregation. Hydrogenation of the samples is done by exposure to atomic hydrogen. The 7×7-reconstructed surfaces are held at a temperature of approximately 400 °C and exposed to 10 000 L hydrogen<sup>15,16</sup> facing a tungsten filament heated to 1800 °C. Since the H:Si(111)-(1×1) surface is practically inert it is possible to process two samples on the same sample holder and then desorb hydrogen from one of the samples to restore a perfect 7×7 reconstruction without affecting the passivated surface. Deposition of gold on both 1×1 and 7×7-reconstructed surfaces at the same time leads to identical coverages. Simultaneous processing and analyzing of the two systems under the same conditions allows a truly comparative study.

### III. RESULTS AND DISCUSSION

#### A. Surface quality

The hydrogenation restores the 1×1 symmetry of the bulk and should destroy the Fermi-level pinning of the 7×7 reconstruction. This has been confirmed for chemically processed samples.<sup>10</sup> From LEED, valence-band and core-level spectra an excellent 1×1 termination is found for samples exposed to atomic hydrogen even at room temperature. Processing of *p*- and *n*-type samples under the same conditions shows that Fermi-level depinning is only achieved for hydrogenation at temperatures around 400 °C, where the process of stacking fault removal is not kinetically limited.<sup>15</sup> The surface quality is illustrated by Si2*p* core-level spectra measured on both surfaces at  $T \sim 30$  K in order to reduce thermal broadening (Fig. 1). On the 7×7-reconstructed surface the large number of inequivalent chemical environments makes the interpretation of the spectra difficult<sup>17</sup> and broadens the identified contributions. The metallicity of this semiconductor surface seen in the valence-band spectra (Fig. 3) leads to a background of scattered electrons fitted by an integral in Fig. 1. This scattering adds an asymmetric broaden-

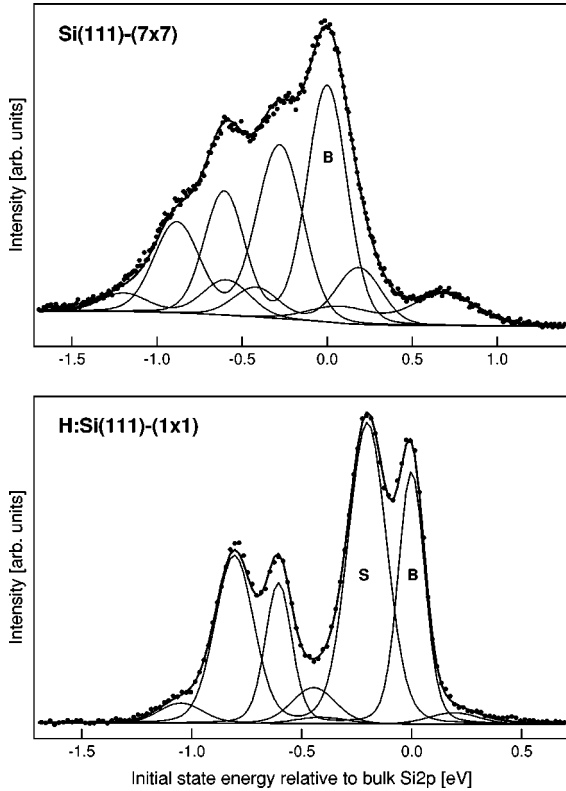


FIG. 1.  $\text{Si}2p$  core-level spectra of  $\text{Si}(111)-(7\times 7)$  and  $\text{H}:\text{Si}(111)-(1\times 1)$  recorded at  $h\nu = 130$  eV and  $T \sim 30$  K with normal photon beam incidence and  $\Theta_e = 45^\circ$  emission angle. The bulk and surface contributions are labeled  $B$  and  $S$ , respectively.

ing to the spectral components. For the hydrogenated surface the high symmetry of the  $1\times 1$  bulk termination gives rise to two narrow  $\text{Si}2p$  doublets identified as a bulk and a surface contribution.<sup>1</sup> This surface is semiconducting as the unpinned surface Fermi-level coincides with the bulk Fermi-level position fixed by the doping. There is no scattered background and the linewidth of the spectral components is remarkably small [130 meV and 190 meV full width at half-maximum (FWHM) for the bulk and the surface component]. Introducing a Lorentzian lifetime broadening  $\Gamma_L \sim 40$  meV and the Gaussian width  $\Gamma_R \sim 40$  meV of the resolution yields a phonon broadening of  $\Gamma_{\text{phonon}} \sim 100$  meV at this temperature.

### B. Auger and valence-band photoemission

The growth mode of gold on  $\text{H}:\text{Si}(111)-(1\times 1)$  and  $\text{Si}(111)-(7\times 7)$  is studied by Auger spectroscopy. Both samples are studied at the same time. The layer-by-layer growth mode for the  $\text{Au}/\text{Si}(111)$  interface is used as a reference to compare relative intensities and coverage. For the  $\text{Au}/\text{H}:\text{Si}(111)-(1\times 1)$  interface the  $\text{Si}(LVV)$  and  $\text{Au}(NVV)$  Auger peak intensities show strong differences (Fig. 2). The linear increase and decrease of the  $\text{Au}(NVV)$  and  $\text{Si}(LVV)$  peak intensities, respectively, point to island growth for gold coverages beyond  $\Theta \sim 0.5$  ML. The  $\text{Si}(LVV)$  splitting for higher gold coverages<sup>18</sup> related to silicon in gold environment is seen for both interfaces. This will be discussed in the following paragraphs. The valence-band spectra of the hydrogenated surfaces (Fig. 3) show the characteristic peaks  $a$

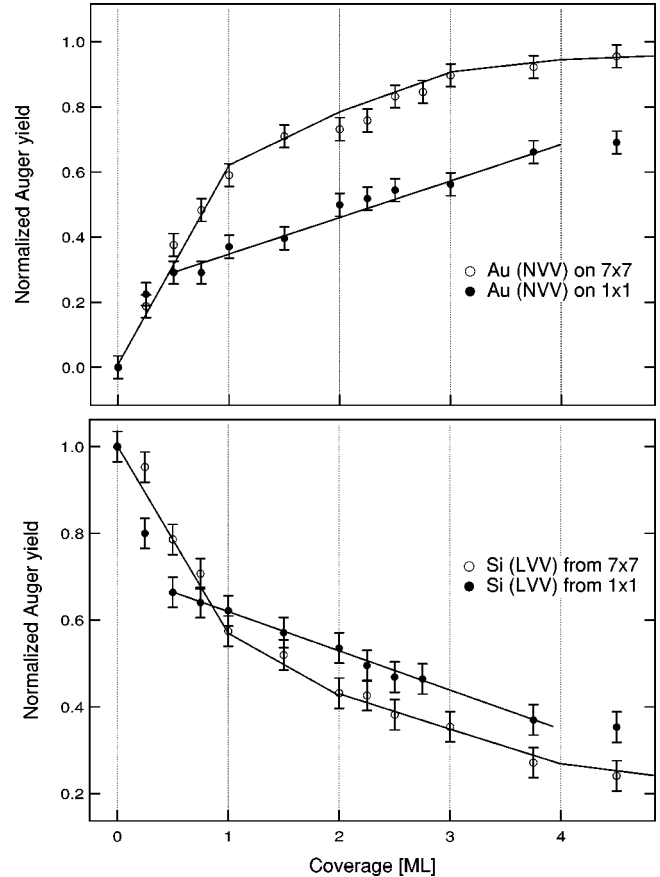


FIG. 2. Auger signal of silicon and gold for different gold coverages on  $\text{Si}(111)-(7\times 7)$  and  $\text{H}:\text{Si}(111)-(1\times 1)$ . Above  $\Theta \sim 0.5$  ML the growth mode on the hydrogenated surface is island type while gold grows in layer-by-layer mode on  $\text{Si}(111)-(7\times 7)$ .

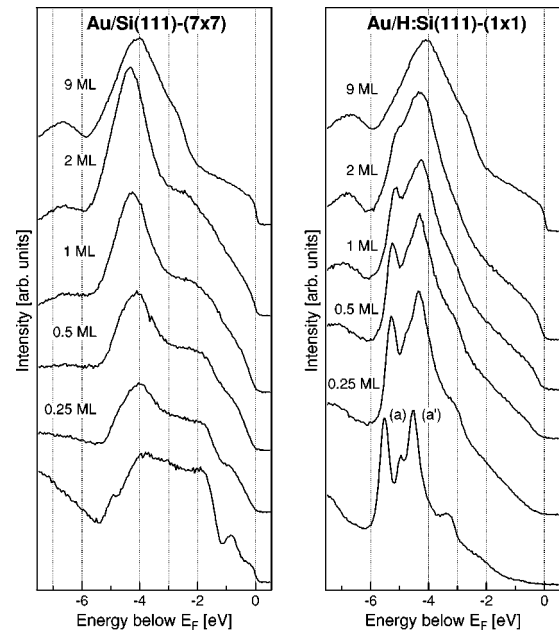


FIG. 3.  $\text{H}:\text{Si}(111)-(1\times 1)$  and  $\text{Si}(111)-(7\times 7)$  valence band at  $h\nu = 17.5$  eV in  $K$  point for different gold coverages. The peak labeled  $a$  attributed to the  $\text{Si}-\text{H}$  bond remains for coverages beyond 2 ML.

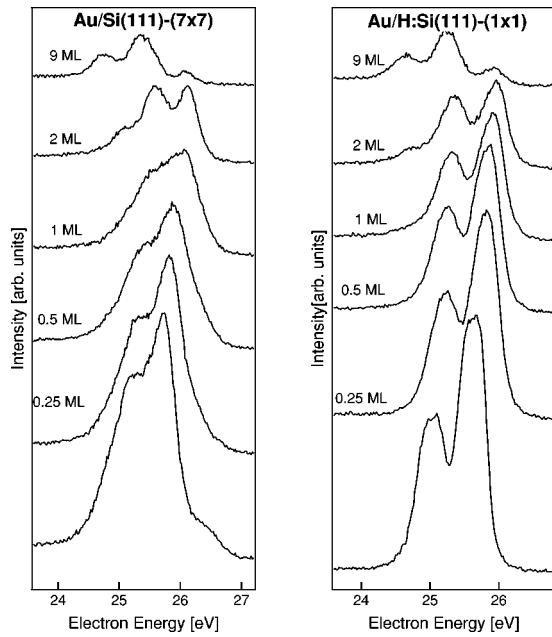


FIG. 4. H:Si(111)-(1×1) and Si(111)-(7×7) Si2*p* core levels recorded in surface-sensitive mode ( $h\nu=130$  eV) for different gold coverages. The appearance of a Si2*p* doublet shifted to higher binding energy is related to silicon segregated on top of the deposited gold film.

and  $a'$  ( $\sim 300$  meV FWHM) attributed to the Si-H bond and to the Si-Si backbond, respectively.<sup>1</sup> On the Si(111)-(7×7) surface the local electronic properties reflected by the valence-band spectra are immediately affected when gold is deposited. For Au/H:Si(111)-(1×1) it is a mere superposition of the valence-band spectra of H:Si(111)-(1×1) and gold. The peak labeled  $a$  is still visible for coverages beyond  $\Theta=2$  ML. This is explained by island growth mode in agreement with the Auger study.

### C. Core-level spectroscopy

High-resolution photoelectron spectroscopy of the Si2*p* and Au4*f* core levels gives information about the chemical environments of silicon and gold. The Si2*p* core-level spectra recorded at  $h\nu=130$  eV with a probing depth of  $\lambda \sim 5$  Å (Fig. 4) were all taken at the same time as the valence-band spectra (Fig. 3). Deposition of gold shifts the Si2*p* core levels to lower binding energies for both interfaces as the Schottky barrier is formed. An additional Si2*p* doublet shifted to higher binding energies appears. It is attributed to silicon segregated on top of the deposited gold film.<sup>19</sup> The position and intensity of this component stabilizes for  $\Theta \leq 2$  ML coverage on Si(111) and  $\Theta \sim 4$  ML coverage on H:Si(111)-(1×1) indicating that the segregated silicon skin is completed. It remains stable for higher gold coverages. The Au4*f* core levels have been studied at the same time. The splitting of the Au4*f* core levels for high gold coverages associated with the delayed onset of a Au4*f* signal from bulk gold below the segregated silicon skin<sup>19–21</sup> has been confirmed for both interfaces. The splitting is already seen for low gold coverages on the hydrogen-terminated surface. This is explained by a larger bulk gold contribution from islands. The growth mode as read from Auger and photoemission

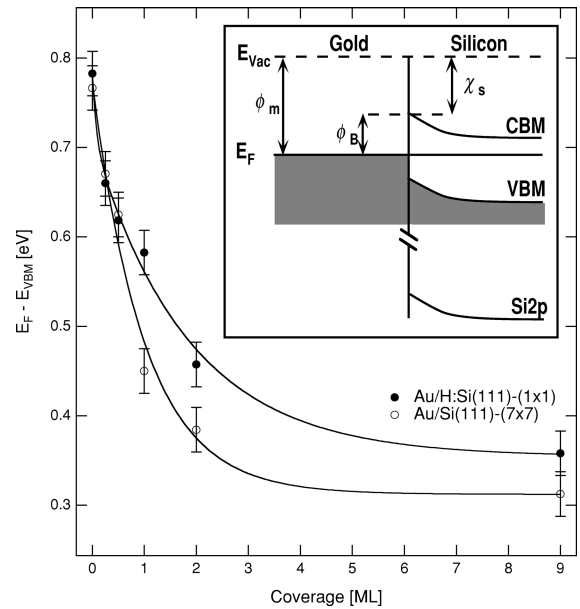


FIG. 5. Position of the Fermi level relative to the valence-band maximum as a function of the coverage. The inset illustrates the relation between the Si2*p* core-level position and the Schottky barrier formation. For the clean surfaces the unpinned Fermi-level position of the H:Si(111)-(1×1) surface (light  $n$  doping) coincides with the pinning of the 7×7 reconstruction.

yield shows that island coalescence is reached for  $\Theta \sim 4$  ML in agreement with the coverage found for the completion of the segregated silicon skin.

### D. Schottky barrier

Schottky barrier formation is monitored by the movement of the Si2*p* core levels after gold deposition. From the inset in Fig. 5 it is seen that the Si2*p* core-level position has to be related to the valence-band maximum. Since both the hydrogenated and the bare 7×7-reconstructed surface are studied at the same time the relative comparison of the Schottky barrier heights is very accurate. Five hydrogenated samples ( $p$  and  $n$  type, different doping levels) have been studied. The measured  $p$ - and  $n$ -type Schottky barriers follow the relation  $E_G = \Phi_{Schottky(n)} + \Phi_{Schottky(p)}$ . The averaged Schottky barrier height is found to be  $\Phi_{Schottky(n)} = 0.75 \pm 0.04$  eV, which is very close to  $\Phi_{Schottky(n)} = 0.81$  eV for Au/Si(111)-(7×7). The evolution of the Schottky barrier with coverage (Fig. 5) shows differences between the hydrogen-passivated and the bare interface for coverages  $\Theta \sim 1-2$  ML.

The Si(111)-(7×7) and the H:Si(111)-(1×1) surface are basically different. While the 7×7-reconstructed surface is highly reactive and very complex the 1×1-terminated surface passivated with hydrogen is a nonreactive model surface. As one might expect the deposition of gold on those surfaces yields different growth modes. On the 7×7-reconstructed surface the reconstruction is immediately affected and surface states disappear. On the nonreconstructed surface passivated with hydrogen the growth mode is clearly three dimensional even if the nucleation process at surface defects for low coverages is not easy to interpret. Surface states related to the 1×1 termination remain visible

for coverages beyond two monolayers. The formation of a segregated silicon skin on top of the deposited gold film is seen for both interfaces. For the bare Au/Si(111) interface this silicon skin is found to stabilize for  $\Theta \sim 2$  ML gold coverage, which is less than half the stabilization coverage found in earlier studies.<sup>19</sup> This confirms that there is practically no intermixing of gold and silicon, neither at the interface nor at the top of the deposited gold. On the hydrogen-terminated surface the film stabilizes at  $\Theta \sim 4$  ML after gold island coalescence. The Schottky barrier height for high gold coverages is very similar for the Au/H:Si(111)-(1 $\times$ 1) and the Au/Si(111) interface. Significant differences are only observed during island growth  $\Theta \sim 0.5-4$  ML. Since there is a strong silicon segregation the hydrogen termination is certainly affected at the island nucleation sites. Assuming an hemispherical island shape the coalescence coverage  $\Theta \sim 4$  ML leads to a mean distance  $\delta \sim 30$  Å between the nucleation sites. Even though some hydrogen remains at the

interface<sup>2,7,3,8</sup> the Schottky barrier height can be the same for the bare and the hydrogen-modified interface. This has been found for interfaces formed with silver.<sup>3,22</sup>

#### IV. CONCLUSION

In conclusion we find from the comparative study of Au/H:Si(111)-(1 $\times$ 1) and Au/Si(111)-(7 $\times$ 7) that hydrogen termination of Si(111) enhances the surface diffusion length and thereby modifies the growth mode of Au/Si(111) from two dimensional to three dimensional. During island growth the electronic properties of the clean and the modified interface differ slightly. Segregation of silicon indicates that the hydrogen passivation is partially destroyed. Island coalescence for higher coverages leads to identical Schottky barrier heights for both interfaces. The estimated density of nucleation sites, which are supposed to supply the segregated silicon, is high enough to force the macroscopic electronic properties to be those of Au/Si(111).

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