Preservation of a 7×7 Periodicity at a Buried Amorphous-Si/Si(111) Interface

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The interface between a silicon (111) substrate and amorphous silicon deposited at room temperature is shown to retain the (7×7) periodicity of the substrate surface. The buried interface was examined by transmission-electron microscopy and diffraction. The interface reconstruction appears to differ from the surface Si reconstruction mainly by the absence of an ordered array of adatoms. If the amorphous-crystalline interface is moved nominally 15 Å by solid-phase regrowth, the 7×7 periodicity is removed. The (100) 2×1 reconstruction is not preserved after amorphous-Si deposition.

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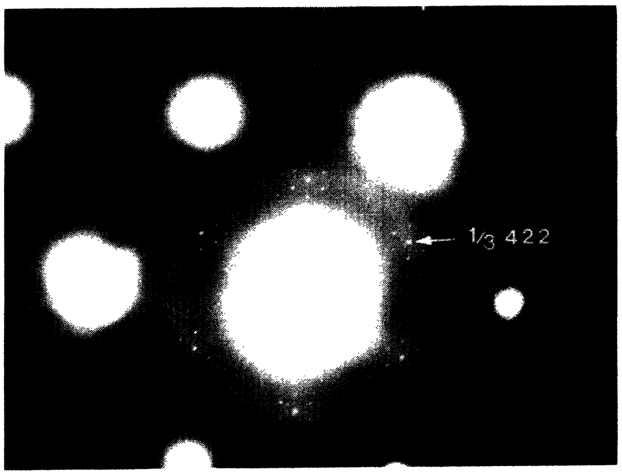
The relationship between atomic structure at the vacuum-solid interface and the solid-solid interface has proved elusive despite considerable activity in both regimes. Studies of adsorbate-induced surface reconstructions (or reordering) begin to bridge the gap in the monolayer range but often cannot be extended to the solid-solid regime. This is because the principal structural tools of the surface scientist, such as low-energy electron diffraction (LEED), are not useful in the examination of structure beyond the first layers of a solid. The recent use of more penetrating probes for both surface science and interfaces is clarifying this issue and firmly establishing a link between these two fields of solid-state science. Interfaces often play a bigger role in the determination of important physical characteristics of solids, particularly semiconductor devices. Therefore, there is a strong desire to relate the results of surface studies to buried interfaces. Transmission electron microscopy is a technique which is capable of studying buried interfaces in thin samples with as much experimental accuracy as surface imaging and diffraction techniques.

In this Letter we will demonstrate for the first time the preservation of the surface periodicity of a substrate underneath a continuous disordered thin film. This is demonstrated by the Si(111)7×7 surface reconstruction whose stability has been indicated previously. Upon adsorption of atomic hydrogen, for example, the 7×7 reconstruction shows only a diminution of the LEED pattern,[1] whereas the Si(100) reconstruction changes from 2×1 to 1×1.[2] (These results are examples of previous studies of surface periodicity preservation at "buried" interfaces which were restricted to monolayer coverages of adsorbates.) Very recently, Rutherford backscattering and channeling as well as LEED have been used to investigate directly changes in the geometry of the Si(111)7×7 and Si(100)2×1 reconstructions upon room-temperature deposition of Si or Ge.[3,4] Channeling allows a characterization of a substrate reconstruction by giving the number of monolayers displaced at the surface from sites of the bulk lattice ("bulklike") as a result of the reconstruction.[5] In the case of Si(111) it was found that this number does not change upon room-temperature deposition of Si or Ge, i.e., the atomic displacements in the surface region associated with the 7×7 reconstruction remain intact, and the 7×7 seems unperturbed. The Si(100)2×1 reconstruction, on the other hand, was shown to reorder completely to a bulklike configuration under the same conditions. X-ray standing-wave interferometry has also been used to examine atomic displacements at related (111) interfaces.[6]

However, neither ion channeling nor standing-wave interferometry is able to identify the presence or absence of a periodic surface structure. We will show in this Letter that the 7×7 periodicity is preserved at the interface between a reconstructed surface and a deposited amorphous Si overlayer. Nevertheless, inspection shows that the structure of the buried surface differs slightly from that of the clean surface. We propose that this difference arises partly from the absence of the periodic array of adatoms believed to be present at the clean surface.[7–9]

Silicon wafers of n type with resistivity 1 Ω cm were cleaned by the Shiraki method[10] just prior to insertion into a molecular-beam-epitaxy chamber with base pressure 10^{-10} Torr. *In situ* cleaning consisted of a 2-min anneal at 820 °C. After a cooling to room temperature Auger electron spectroscopy indicated clean surfaces, and sharp LEED patterns characteristic of the 7×7 [see Fig. 1(a)] and 2×1 reconstructed surfaces were seen for (111) and (100) wafers, respectively. Silicon was subsequently deposited by electron-beam evaporation to a thickness of either 50 or 70 Å at a rate of 1 Å/s. No LEED pattern was observable after deposition, indicating the disordered nature of the overlayer, in accordance with previous results.[4] For examination by transmission electron microscopy (TEM), samples were transferred in air and either chemically thinned in plan view or ion thinned in cross section. During chemical thinning, the amorphous

(a)



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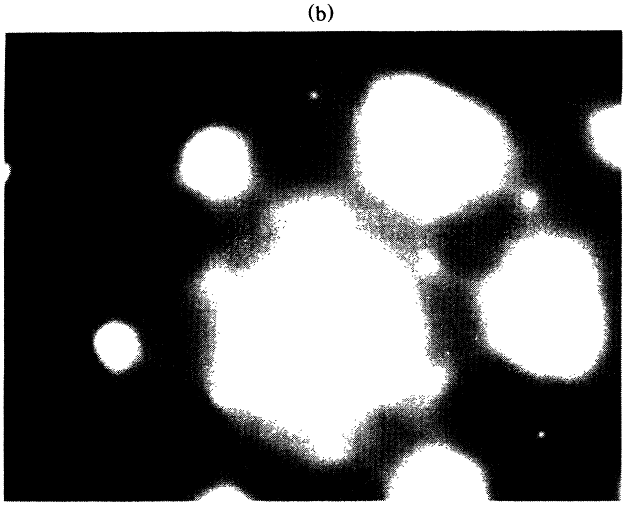

(c)

FIG. 1. (a) LEED pattern from a clean Si(111)7×7 surface just prior to deposition of Si at 300 K. Recorded at normal incidence with 62-eV electrons. (b) High-energy (200 kV) transmission electron diffraction pattern from the same surface shown in (a) after deposition of 70 Å of amorphous Si at 300 K. The sample was transferred through air, and almost all of the Si substrate was removed chemically before TEM examination. (c) High-energy transmission electron diffraction pattern from the sample in (b) after *in situ* annealing which would be expected to cause partial regrowth of the amorphous-Si/crystalline-Si interface. The 7×7 ordered structure has disappeared.

layer was protected by coating of the front surface with beeswax. TEM was performed with either a JEOL 200CX instrument operating at 200 kV or a JEOL 4000EX instrument operating at 400 kV with point resolution 1.8 Å. Imaging and diffraction were performed in both plan-view and cross-section geometries.

Figure 1(a) shows the LEED pattern obtained from a (111)7×7 silicon surface prior to room-temperature deposition of 70 Å of silicon. Figure 1(b) is a high-energy transmission electron diffraction pattern from the same wafer, after Si deposition at 300 K, and after most of the silicon substrate has been removed chemically. In the area (about $1\times1\mu m^2$) from which this diffraction pattern is taken, approximately 1000 Å of Si substrate remains, i.e., the thinning procedure leaves the interface region unchanged. In the diffraction pattern the substrate-crystal diffraction spots, the diffuse rings from deposited amorphous Si, and a 7×7 diffraction pattern which is presumed to come from the amorphous-crystal boundary are all seen. In areas of the sample where amorphous Si was not deposited or had been removed, no 7×7 pattern is observable, and only very weak scattering at the $\frac{1}{3}\langle422\rangle$ [LEED index of type (1,0)] positions is visible. This confirms that the 7×7 periodic structure does not come from the chemically cleaned back surface of the sample. Furthermore, samples which had been annealed at 500 °C for 1 h, which is nominally sufficient to induce 15-Å regrowth of the amorphous Si,[11] no longer showed a 7×7 diffraction pattern, suggesting that the 7×7 ordered interface is metastable. This can be compared with the ion-channeling results which show that the Si(111)7×7 reconstruction reorders to a bulklike configuration if deposition of Ge is carried out at temperatures above 570 K.[3] Figure 1(c) shows an example of the effect of *in situ* annealing of a thin sample under conditions which should cause partial regrowth of the amorphous layer. The amorphous-silicon diffraction rings are still present, but the 7×7 diffraction pattern has disappeared. Nevertheless, the $\frac{1}{3}\langle422\rangle$ diffraction spots are, if anything, more strongly visible, indicating that the regrown amorphous-silicon/crystalline-silicon interface is relatively flat and free of strain. These properties make it a potentially good system in which to study at high resolution the regrowth process. After annealing at higher temperatures almost complete regrowth of the amorphous silicon occurs, and the diffraction pattern shows only a 1×1 periodicity. This is presumably because of oxidation and contamination of the original amorphous Si surface, which can only be removed at higher temperatures. As an interesting aside, the quality of the starting LEED pattern was reflected in the TEM 7×7 diffraction pattern of an as-grown sample. A decrease in intensity of fractional-order LEED spots due to gas absorption (surface contamination) was mirrored in the relative intensities in TEM diffraction.

In comparison, (100) surfaces, which exhibited 2×1 reconstructions prior to deposition of amorphous Si, did not reveal a 2×1 periodic structure in the high-energy transmission electron diffraction patterns after amorphous Si deposition. This is in agreement with the channeling observations which indicated the absence of reconstruction at this interface.[3,4] However, it should be noted that the absence of diffraction spots in the high-energy case only implies the absence of periodic displacements with strong components in the plane of the surface and is quite insensitive to vertical displacements. The channeling measurements, on the other hand, clearly show that the Si(100)2×1 reorders upon room-temperature deposition, i.e., that the atoms of the substrate at the interface occupy bulklike positions within ≈ 0.1 Å.

The 7×7 structure seen at the amorphous-Si/Si(111) interface can also be studied at high resolution in both plan-view and cross-section geometries. Plan-view images reveal that the reconstruction covers essentially all of the interface area. In cross-section geometry one can potentially study the detailed atomic arrangements in the reconstructed layers. However, these images can be interpreted reliably only by image simulation and modeling,[12] which will be reported elsewhere. Figure 2 shows an example of one such image taken at 400 kV in the [112] projection which reveals the buried reconstruction in cross section. The 7×7 periodicity is not clearly seen in such images, possibly as a result of projection through different domains. Nevertheless, at the interface in this and other images there appear to be at least two disturbed double layers which exceeds the number expected from at least one recent model,[9] when adatom layers are ignored (to be discussed later). This may be the result of some "epitaxial" growth of the first deposited layers of amorphous Si; indeed, in some places several other layers in partial registry with the substrate are seen, a finding also made in recent studies of amorphous Si grown on clean Si substrates.[13] Detailed interpretation is dependent on image simulation and more experiment.[12] In cross-section preparation, samples were also exposed to temperatures approaching 200 °C and to low-energy ion bombardment which may lead to changes in the interface structure.

While the periodicity of the diffraction pattern in plan view is identical to the periodicity seen from clean surfaces, differences in the intensity distributions among the fractional-order spots are observed.[8,9,14–16] In particular, only spots along the lines joining 1×1 (e.g., $\frac{1}{3}\langle 422\rangle$) diffraction spots can be seen, and of these, the six spots adjacent to the latter are strongest. This diffraction pattern is consistent with the triangle-dimer model in the absence of an ordered array of adatoms.[8] The adatoms and dimers are responsible for intense fractional-order spots midway between 1×1 beams.[8,14] It is quite reasonable to assume that the deposition of amorphous Si disorders the periodic array of adatoms which is believed to exist on the clean Si 7×7 surface.[7] It is also expected that the remaining structure is very similar to the clean surface, although details such as the presence of dimers can be determined only from extensive analysis of diffraction and image intensities. The stacking-fault and vacant corner sites now believed to exist in the 7×7 structure are most likely responsible for the stability of this structure on room-temperature Si deposition. Some image areas in cross section show faulted layers which may have epitaxially grown on the reconstructed surface.

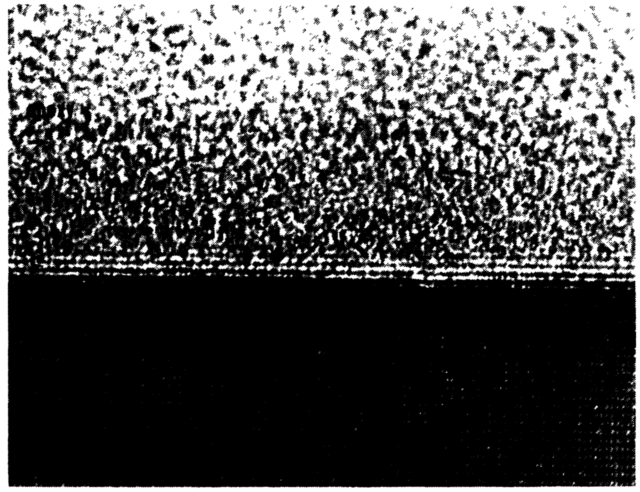

FIG. 2. A high-resolution transmission electron image taken at 400 kV of the amorphous-Si/crystal-Si interface whose diffraction pattern is shown in Fig. 1(b). The sample was thinned in cross section in the [112] direction, and the image is taken near the Scherzer focus where the atoms in thin areas are dark. The amorphous-crystal interface, which shows at least two selvedge double layers associated with the 7×7 reconstruction, and the amorphous-Si surface which is bounded by epoxy resin are arrowed. The former selvedge layers can be identified because of their position relative to the black and white fresnel fringe at the termination of the bulk crystal.

The major point of this paper is the observation of a superstructure at a solid-solid interface which has heretofore only been associated with a solid-vacuum interface. The implications of this finding are that much of the knowledge provided by surface science may also be applicable to solid systems. For example, the atomic and electronic structure associated with a surface reconstruction may be an appropriate description of some properties of grain boundaries. Questions of epitaxy and epitaxial regrowth (briefly discussed here) may be influenced by the interface structure.

Passivating layers (e.g., the Si/SiO_2 interface) may partly preserve the structure of the original surface and thus influence the electronic structure associated with these interfaces. Finally, the preservation of surface structures at buried interfaces may also play a direct role in the epitaxial relation of an overlayer and a substrate: For example, the novel orientations of $NiSi_2$ on Si(111) [17] may possibly be related to faulted and unfaulted parts of the 7×7 surface.

Clearly the preservation of part of the 7×7 periodic structure on a clean Si(111) surface at the interface with a deposited amorphous layer is also significant in that it allows the study of such reconstructions by techniques which are not compatible with UHV surface science. We present an identification of a periodic structure only a few monolayers in extent at a buried interface between a thin film and a substrate. Indeed, this is the first observation of such an interfacial superperiodic structure to our knowledge, although there have been elegant diffraction studies of Au grain boundaries[18] which have shown that atomic rearrangements occur where the periodicity is that of the coincidence site lattice of the two crystals. Transmission electron microscopy is ideally suited to the study, not only of clean surfaces,[8,14–16] but of buried periodic structures also. The latter are not amenable to purely surface-sensitive techniques but are obviously of considerable importance in solid-state physics.

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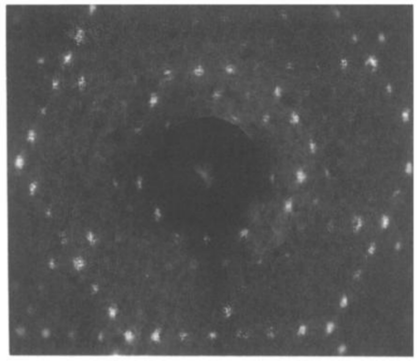

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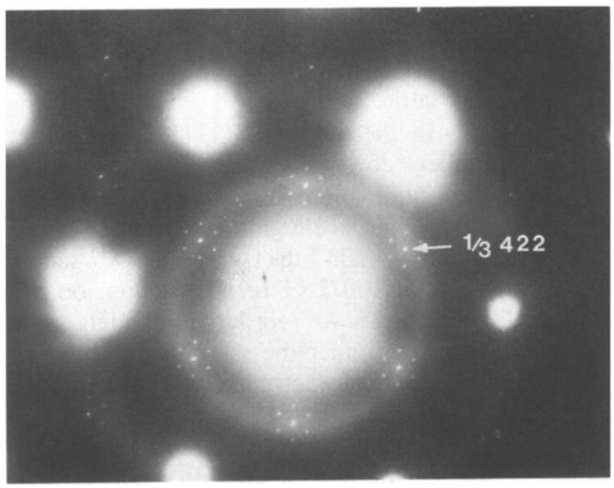

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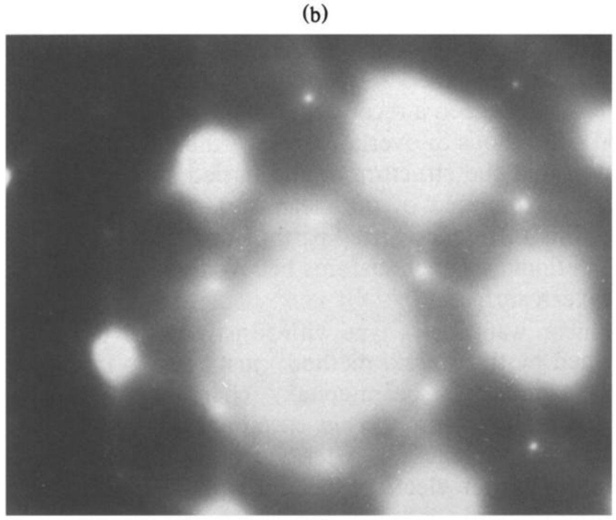

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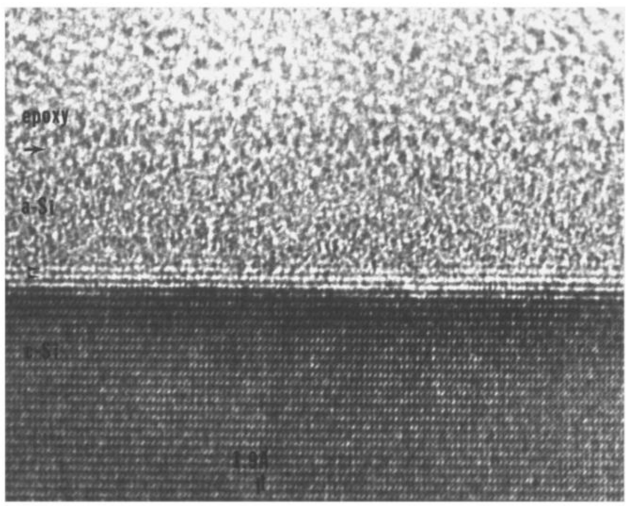

FIG. 2. A high-resolution transmission electron image taken at 400 kV of the amorphous-Si/crystal-Si interface whose diffraction pattern is shown in Fig. 1(b). The sample was thinned in cross section in the [112] direction, and the image is taken near the Scherzer focus where the atoms in thin areas are dark. The amorphous-crystal interface, which shows at least two selvedge double layers associated with the 7×7 reconstruction, and the amorphous-Si surface which is bounded by epoxy resin are arrowed. The former selvedge layers can be identified because of their position relative to the black and white fresnel fringe at the termination of the bulk crystal.