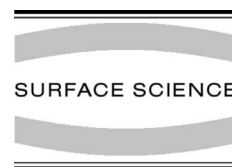




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Phase transition and stability of Si(1 1 1)– $8 \times '2'$ -In surface phase at low temperatures

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Abstract

Scanning tunneling microscopy (STM) has revealed several intermediate stages during a phase transition from the Si(1 1 1)- 4×1 -In surface phase to the $8 \times '2'$ -In phase by cooling below room temperature, showing a gradual and inhomogeneous redistribution in surface electronic density, and also the influence of impurity adatoms. By depositing tiny amounts of adsorbates (less than 0.05 ML of group III atoms or about 0.1 ML of Ag atoms) on the low temperature (LT) $8 \times '2'$ -In phase at around 100 K, the surface reverted to the high-temperature 4×1 -In phase, accompanied with an increase in electrical conductivity. LT STM observations showed that the deposited Ag atoms locally destroyed the $8 \times '2'$ -In phase, while the deposited In atoms totally destroyed the phase to return the surface wholly into the 4×1 -In phase. Such a quenched 4×1 -In phase at LT was quite stable against further adsorptions of these impurity atoms. These results suggest that the impurity atoms act as ‘perturbers’ which electronically disturb the $8 \times '2'$ phase to revert to the 4×1 phase. In other words, the phase transition of the 4×1 -In \rightarrow $8 \times '2'$ -In by cooling is electronically driven. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Indium adsorption on the Si(1 1 1) surface is known to lead to a number of surface reconstructions [1]. Especially, a Si(1 1 1)- 4×1 -In surface phase at about one monolayer (ML) of In coverage attracts much attention recently, which

possesses quasi-one-dimensional (1D) nature in atomic arrangement and electronic structure. Since Lander and Morrison [2] first observed this phase in 1964, the 4×1 -In phase has been studied by various surface-sensitive techniques as described in Ref. [3]. Nevertheless, its atomic structure still remains a topic of debate [4,5]. Recently, a reversible phase transition from the 4×1 -In phase into a $8 \times '2'$ -In phase around 130 K was discovered [6], which was characterized by a Peierls-like transition due to its quasi-1D metallic nature in the surface electronic states. The notation $\times '2'$ means an

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incomplete long-range order of the double periodicity across the 1D chains, so that only half-order streaks appear in diffraction patterns instead of half-order spots. Another aspect of this phase transition is discussed in terms of a Fermi-liquid to Luttinger-liquid transition [7,8].

In the present work, we pay our primary attention to the structural and electrical properties of the Si(111)- 8×2 -In surface phase at low temperatures (LT) in order to clarify the nature of the $4 \times 1 \rightarrow 8 \times 2$ phase transition. Especially the influences of additional adsorbates on the surface phases are investigated to modulate the surface electronic states.

2. Experiments

Experiments were carried out in an ultrahigh vacuum (UHV) chamber with a base pressure of about 2×10^{-10} Torr, equipped with LT-scanning tunneling microscopy (LT-STM, UNISOKU USM 501 type) and reflection-high-energy electron diffraction (RHEED) systems. The substrates used were B-doped Si(111) wafers with a resistivity of $\approx 0.01 \Omega\text{cm}$. Atomically clean Si(111) surfaces were prepared in situ by direct Joule heating at 1500 K after outgassing at 800 K for several hours. After this treatment, a sharp 7×7 -RHEED pattern was observed at room temperature (RT), and STM images corresponded to a well-ordered Si(111)- 7×7 clean surface. The Si(111)- 4×1 -In surface was produced by In deposition onto the 7×7 substrate kept at 700 K by direct current heating. Then, the sample was cooled down to RT and transferred to the cold STM stage. Small amount of Ag and In atoms were additionally deposited on top of the surface at 70 K on the LT-STM stage. For STM observations, electrochemically etched tungsten tips were employed after cleaning by in situ heating in UHV. All STM images were taken in constant-height mode.

For electrical resistance measurements, another UHV chamber was used, equipped with RHEED and a sample holder for cooling by liquid nitrogen. An n-type Si(111) wafer of 50–100 Ωcm resistivity was used. The surface preparations were the same as for STM observations. During metal–atom de-

positions under isothermal conditions at LT, the electrical resistance of the wafer was measured as a voltage drop between a pair of Mo wire contacts (0.3 mm in diameter) about 5 mm apart each other, pressed on the front face of the wafer, with constant current fed through the substrate clamps at the both ends [9]. The quality of the electrical contact between the substrate and electrodes was confirmed by observing a linear relation between voltage signal and electrical current in 0–90 μA range. Differential resistances were obtained by changing the measurement current to eliminate thermovoltage and photovoltage effects at the electrode contacts.

The amounts of deposited metals were determined by deposition durations with keeping constant deposition rates with a calibration that the saturation coverages for the $\sqrt{3} \times \sqrt{3}$ superstructures are 1/3 ML for Al, Ga, and In, and 1 ML for Ag on a Si(111) surface.

3. Results and discussion

3.1. Transition from the 4×1 -In to 8×2 -In phase

Fig. 1 shows a series of filled-state STM images at the phase transition from the 4×1 -In to 8×2 -In phases obtained at ≈ 70 K. The 4×1 periodicity is clearly seen on each stripe in Fig. 1(a), the unit cell of which is shown by solid lines. Each stripe can be divided into two sub-chains, left and right sub-chains. Protrusions in some sub-chains become brighter for every second unit cell, resulting in formation of the ' $\times 2$ ' periodicity along the sub-chains, while the other sub-chains remain the ' $\times 1$ ' periodicity. The double-periodicity modulation is pronounced only at some portions in the image. The ' $\times 2$ ' super-periodicity is thus formed inhomogeneously.

Fig. 1(b) shows an image of other area on the same sample at the same temperature, which may correspond to the next stage of the phase transition, where the ' $\times 2$ ' periodicity along stripes is more clearly visible. Although the protrusions with the double periodicity along stripes are pronounced, smaller protrusions between the pronounced ones are still visible as shown in a line

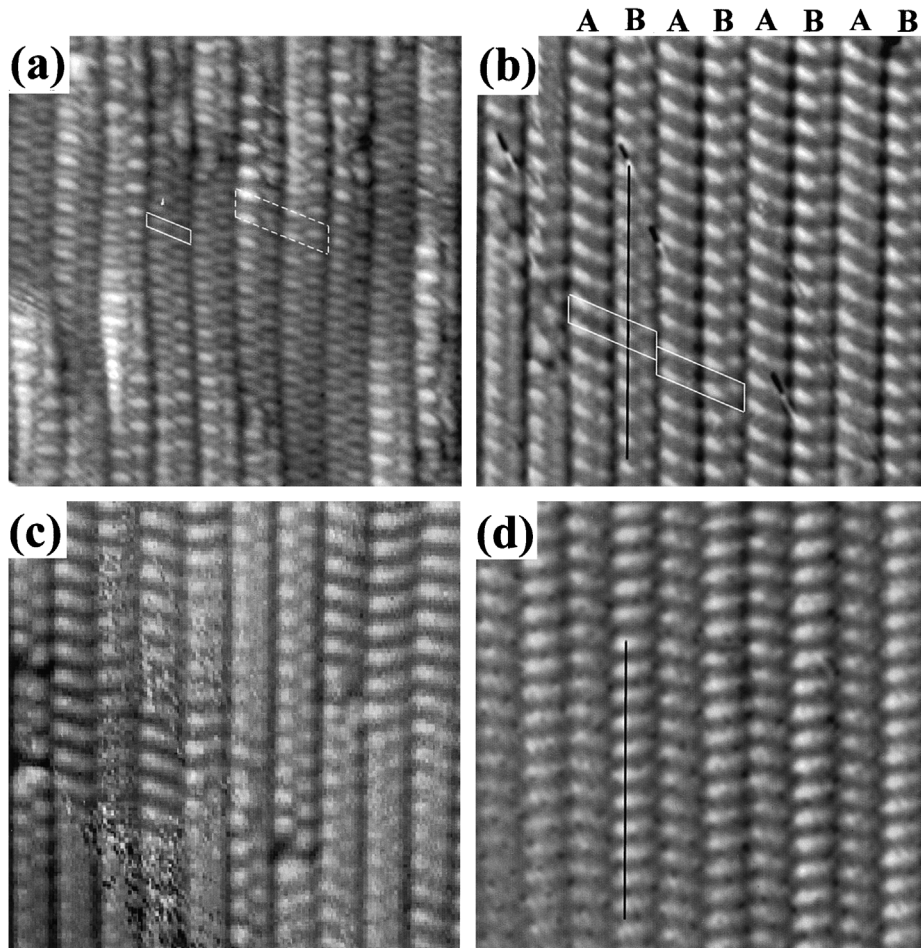


Fig. 1. Filled-state STM images ($135 \times 135 \text{ \AA}^2$) on the same specimen surface at $\approx 70 \text{ K}$, showing an inhomogeneous formation of the 8×2 -In phase from the 4×1 -In phase. The bias voltages are (a) 1 V, (b) 2 V, (c) 1 V, and (d) 1 V, respectively. In (a), a parallelogram by solid lines indicates an unit cell of the 4×1 superstructure, while dashed lines indicate that of the 8×2 superstructure.

profile (Fig. 2(a)) along a line indicated in Fig. 1(b). The ' $\times 8$ ' periodicity across the stripes is now recognized clearly in Fig. 1(b); the stripes indicated by 'A' and 'B' show slightly different features in the ' $\times 2$ ' protrusions on stripes, which are alternately arranged to make the ' $\times 8$ ' periodicity across the stripes. At the same time it is noted that the 8×2 unit cells on some stripes are shifted roughly by a half of the ' $\times 2$ ' periodicity on the neighboring stripes, as shown by unit cells drawn in Fig. 1(b).

The other area on the same sample shows an image of Fig. 1(c), where the protrusions showing

the ' $\times 2$ ' periodicity are more pronounced while minor protrusions in-between become less clearly observable than in Fig. 1(b). At the same time, it is noted that some of the ' $\times 2$ ' periodicity along the stripes consist of different features; protrusions in the both sub-chains in some stripes are connected each other while they are separated on other stripes. In this image, the ' $\times 8$ ' periodicity across the stripes is not recognized clearly. Fig. 1(d) may be the complete 8×2 -In phase where each stripe has the ' $\times 2$ ' periodicity consisted of elongate protrusions connecting between the sub-chains in each stripe. The ' $\times 8$ ' periodicity is recognized as

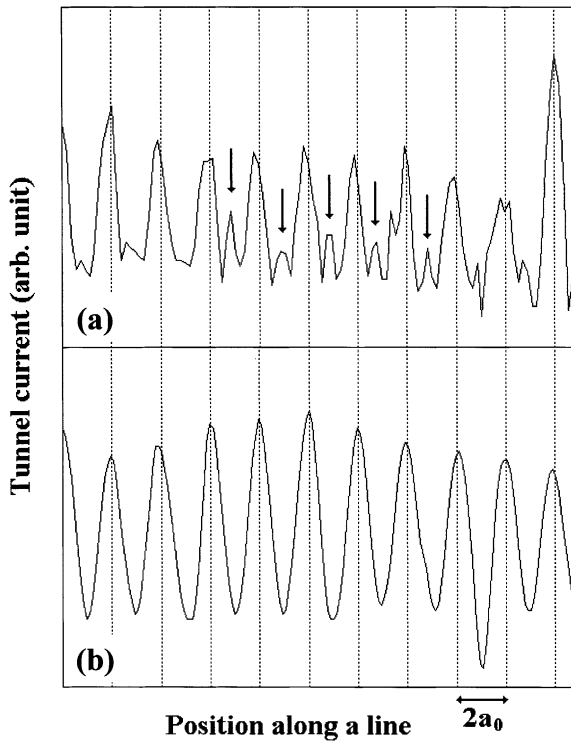


Fig. 2. Profiles along lines indicated in (a) Fig. 1(b) and (b) Fig. 1(d) on a stripe, respectively. Grid lines indicate the double periodicity along the stripes. In (a), the arrows indicate minor protrusions between the major ' $\times 2$ ' modulation along the stripe.

different inclinations of the elongated protrusions on the stripes alternately. A profile along the black line in Fig. 1(d) is shown in Fig. 2(b) where the double periodicity is clearly observed without the in-between minor protrusions.

In this way, the STM reveals gradual and inhomogeneous redistributions of electronic density at the 8×2 phase formation, though the RHEED patterns show a clear 8×2 periodicity as shown in Fig. 3(a). The half-order streaks (indicated by black arrows) come from the modulations in ' $\times 2$ ' periodicity along each stripe without their long-range order across the stripes; the double-periodicity modulation is well in long-range order along each stripe, while it is not in phase between the adjacent stripes. In contrast, the $1/8$ th fractional spots (indicated by white arrowheads) are sharp, indicating that the features in the double-period-

icity modulation along each stripe are different alternately across the stripes, resulting in a long-range ' $\times 8$ ' periodicity across stripes. This result seems consistent with a continuous change in the intensity of the half-order streaks in X-ray diffraction pattern [7] during this transition, indicating a gradual atomic relaxation between the two phases.

3.2. Influence of additional adsorbates

We monitored variations in RHEED pattern during depositions of small amounts of adsorbates on top of the 8×2 -In surface at LT (about 100 K). After deposition of a tiny amount of In atoms (approximately 0.05 ML), the 8×2 -In phase was suddenly transformed to a 4×1 phase, as shown in Fig. 3(b); the half-order streaks and the $1/8$ th fractional-order spots in Fig. 3(a) completely disappeared, remaining the $1/4$ th spots only (indicated by black arrowheads). Similar results were also obtained during depositions of tiny amounts of Al and Ga atoms onto the 8×2 -In surface at LT. In case of Ag deposition, the change was slightly different; the 8×2 pattern gradually faded out, remained up to 0.2 ML coverage of Ag. Beyond this coverage the pattern changed into the 4×1 structure. The 4×1 -RHEED patterns (such as Fig. 3(b)) obtained after these additional depositions of the adsorbates at LT were apparently the same one as that of the pristine 4×1 -In surface at RT.

These results were also confirmed by STM. Fig. 4 shows the STM images after deposition of 0.1 ML of In (Fig. 4(a)) and 0.1 ML of Ag (Fig. 4(b)) on the 8×2 -In surface at ≈ 70 K, respectively. It is seen that the double-periodicity modulations on the stripes hardly observed in Fig. 4(a), resulting in the 8×2 phase disappearing, while the 8×2 phase is partially preserved in Fig. 4(b). Some clusters are seen in both of Fig. 4(a) and (b), which are presumably the additionally deposited In and Ag atoms, respectively. The double-periodicity modulation seems to be suppressed only near the Ag clusters in Fig. 4(b), while the modulation is totally gone away in Fig. 4(a). Traces of the modulation were observed up to 0.4 ML coverage

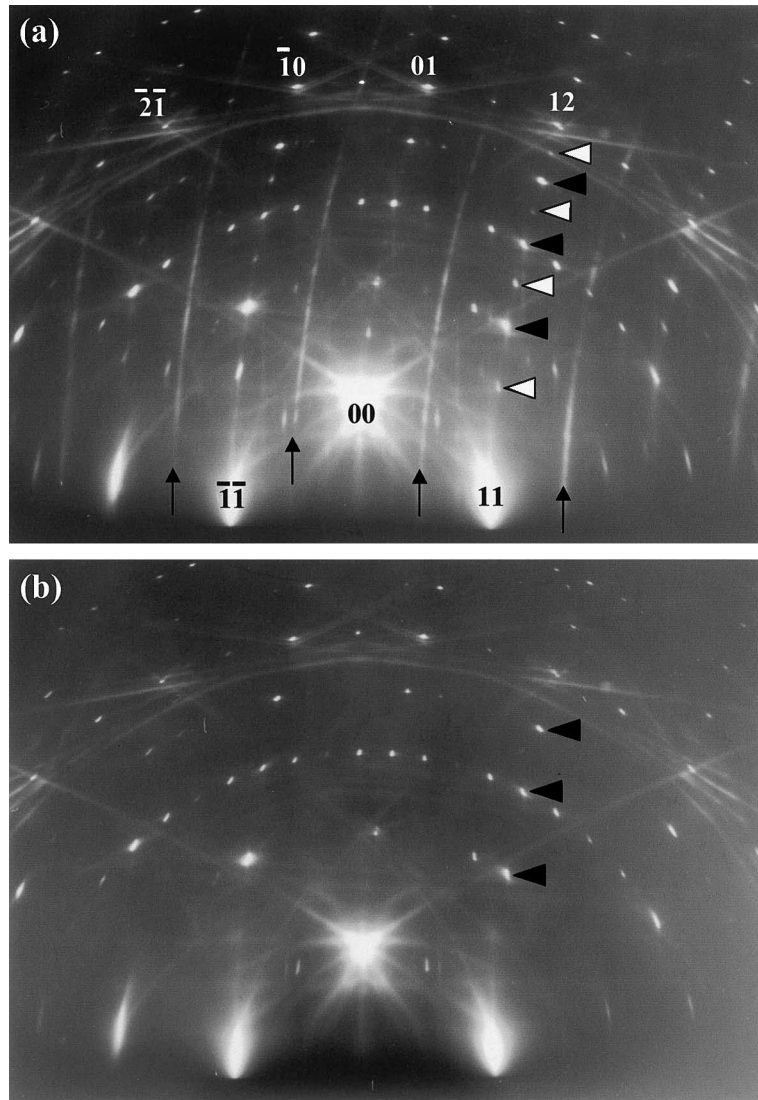


Fig. 3. RHEED patterns of (a) the Si(111)- 8×2 -In phase at ≈ 100 K, and (b) the quenched 4×1 -In phase that was transformed from the 8×2 -In phase by depositing 0.1 ML In on top of it at ≈ 100 K. This ' 4×1 ' pattern looks identical with the pristine 4×1 -In phase at RT.

in Ag deposition, while it disappeared completely only with less than 0.05 ML coverage for In deposition. In this way, the influence of adsorbates upon destroying the 8×2 phase is different from species to species.

And it should be stressed here that very small amounts of In (less than 0.1 ML) are enough to destroy the 8×2 phase totally, suggesting a long-range influence of the adsorbates, or a collective

influence by electronic disturbance. For example, if the 8×2 phase is a charge-density wave (CDW) phase due to a nesting in the Fermi surface as proposed in Ref. [6], the additionally deposited In atoms may destroy the nesting condition by changing the band filling due to charge transfer between the adsorbates and the surface-state bands. Photoemission studies are necessary to verify such a speculation.

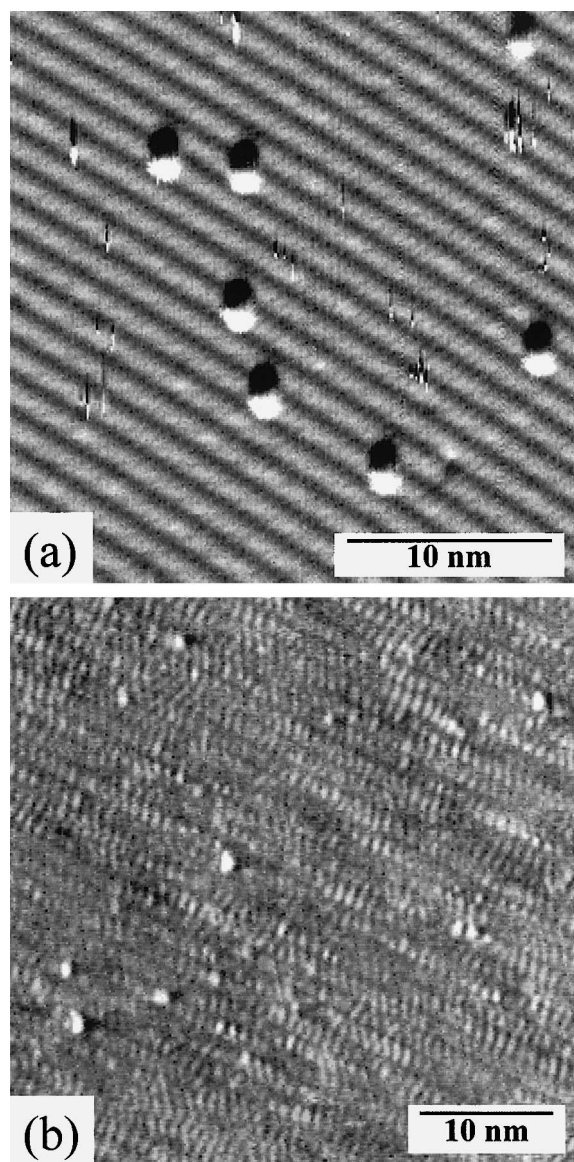


Fig. 4. Filled-state STM images (with 2 V bias voltage) of the Si(111)- 8×2 -In surface after deposition of about 0.1 ML of (a) In and (b) Ag, respectively, at ≈ 70 K.

3.3. Stability of the 4×1 -In surface phase

The RHEED assessment of stability of surface structures against overlayer depositions is based on a natural assumption that, in case of stable surface superstructures, the intensities of both

of fundamental and fractional-order reflections should decrease simultaneously with approximately equal rates during deposition of overlayers. In case of disruption of the surface superstructures during overlayer growths, on the other hand, the fractional-order reflections should fade away more rapidly than the fundamental reflections.

We have done such RHEED measurements about the stability of the quenched 4×1 -In phase at LT (about 100 K) with further deposition of Ag, Al, In, and Ga after the 8×2 -In phase is destroyed by small amounts of these adsorbates. We have monitored the decreases in normalized intensity of the fundamental and quarter-order RHEED spots with the depositions using a 16-bit CCD camera. The results are presented in Fig. 5. One can see that both of the fundamental and fractional-order spots of the ' 4×1 ' pattern attenuate simultaneously with similar rates for the respective adsorbate species, preserving the initial intensity distribution among spots in the patterns. This result indicates that the 4×1 framework is tough against the overlayer depositions, which is a sharp contrast to the 8×2 phase that is not resistant to even tiny amounts of the adsorbates as described in the previous subsection. The pristine 4×1 -In superstructure at RT was also confirmed to be tough with such overlayer depositions.

It was recently demonstrated that the substrate Si atoms in the 4×1 -In phase reconstruct themselves with the 4×1 periodicity [10]. RHEED analyses in Fig. 5 suggest that such a substrate reconstruction is preserved at the overlayer growths, meaning that the reconstruction is preserved at the interface between the overlayer and substrate at LT depositions.

3.4. Resistance measurements

Fig. 6 shows the changes in resistance of the Si crystal (normalized with the initial resistance) during (a) Ag and (b) In depositions on the Si(111)- 8×2 -In surface at ≈ 100 K. At the initial stage of Ag adsorption, the resistance decreases gradually by about 12% with 0.3 ML coverage, which corresponds to the gradual change in surface structure from 8×2 to 4×1 described in the

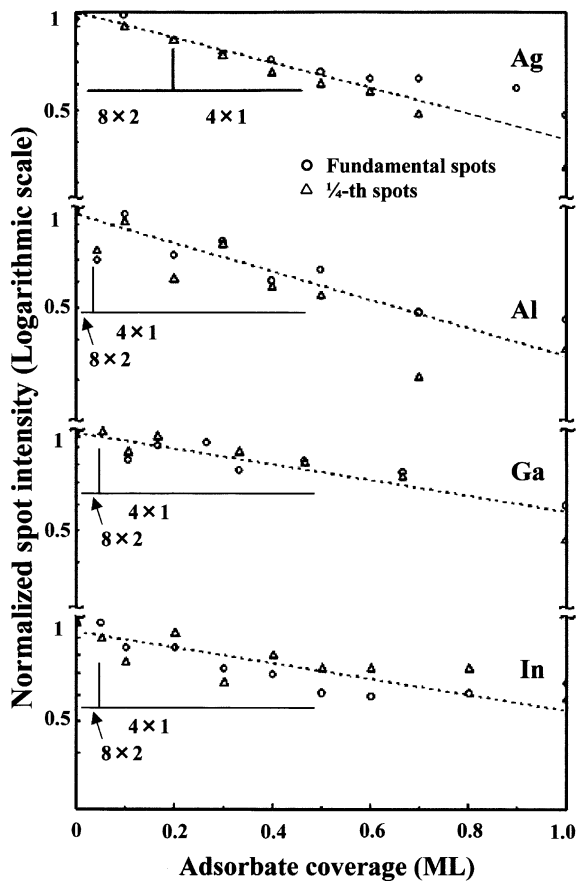


Fig. 5. Changes in diffraction-spot intensity in RHEED patterns during Ag, Al, Ga and In depositions on top of the Si(111)- 8×2 surface at LT (about 100 K). The circles represent the fundamental $(-1,0)$ spots and triangles represent the fractional-order $(-3/4,0)$ spots. The intensities are plotted in logarithmic scale.

previous sub-sections. In contrast, with In adsorption the resistance drops immediately at the beginning, corresponding to the abrupt destruction of the 8×2 phase. The amounts of resistance drops are nearly equal for both cases. After roughly 1 ML depositions, the resistances show temporal increases, but decrease with further depositions for both species. The temporal increases in resistance correspond to the disappearance of the 4×1 phase, leaving only the fundamental spots in RHEED.

The changes in resistance observed here are not inconsistent with the CDW interpretation of the

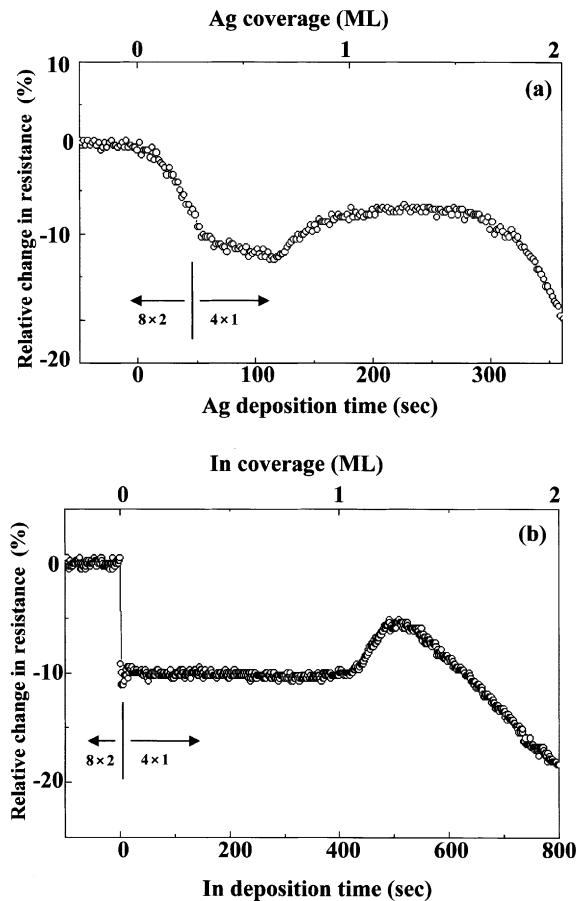


Fig. 6. Changes in resistance of the Si crystal during LT (about 100 K) Ag (a) and In (b) depositions onto the Si(111)- 8×2 -In surface, respectively. The deposition rates of Ag and In were 1/3 and 0.15 ML/min.

8×2 phase [6]. As revealed in photoemission spectroscopy, an energy gap seems to open up in surface-band structure at the 8×2 phase at LT [6], while the 4×1 -In phase at RT has metallic surface states [11]. Therefore, the electrical conductivity through the surface-state bands, if any, is expected to be lower at the 8×2 phase than at the 4×1 phase. The structure transformation from the 8×2 phase to the 4×1 phase by adding small amounts of In or Ag atoms may correspond to restoring the metallic surface states, leading to the decrease in electrical resistance. On the other hand, the most recent Si 2p core-level photoemission spectroscopy reveals that the 8×2 phase is

not semiconducting completely, rather still has a weak metallic character [8]. From this fact, the possibility of a Luttinger-liquid character of the 8×2 phase is discussed, compared with the Fermi-liquid nature of the 4×1 phase [8]. Such a discussion is again not inconsistent with the resistance changes observed here. In any case, we need photoemission spectroscopy measurements about band bending as well as surface-state band structure to clarify the reason for the changes in electrical resistance observed here.

4. Conclusion

We have used STM, RHEED and electrical resistance measurements to study the Si(111)- 8×2 -In surface phase at LT. During the transition from 4×1 -In to 8×2 -In with cooling below RT, the redistribution of the electronic density occurred gradually and inhomogeneously. The 8×2 -In phase was very fragile with small amounts of adsorbed impurities; depositions of less than 0.05 ML of group III metals led to an abrupt destruction of the 8×2 phase, reverting to the 4×1 phase. In case of Ag adsorption on the 8×2 surface, the 8×2 phase was preserved up to about 0.4 ML coverage, resulting in a gradual change into the 4×1 structure; the $\times 2$ modulation along stripes was observed locally by STM during the gradual change. Such changes in structure by adding the ‘perturbers’ induced drops in surface electrical resistance. This may correspond to a recovery of the metallicity in surface-state band structure at the transition from the 8×2 to 4×1 , which should be verified by the future electronic-state analyses. Although the 8×2 phase was very sensitive to the additional adsorbates, the 4×1 reconstruction was much tougher with overlayer growths on it; the 4×1 reconstruction was preserved at initial stages of Ag and group III metal adsorptions up to around 1 ML coverages.

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