

Phonon and polarized reflectance spectra from Si(111)-(4×1)In: Evidence for a charge-density-wave driven phase transition

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The $(4\times 1)\rightarrow(4\times "2")$ phase transition of the In terminated Si(111) surface around 120 K has been investigated by optical spectroscopy. Characteristic surface phonon modes of the 4×1 and $4\times "2"$ phases are observed with Raman spectroscopy. Reflectance anisotropy spectroscopy (RAS) reveals a splitting of a large feature in the optical anisotropy at 2 eV on formation of the low temperature phase. The changes in the RAS and Raman spectra are discussed within the framework of the conflicting models of the phase transition. Charge density wave formation driven by a Peierls transition is favored over transitions involving significant structural modifications.

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I. INTRODUCTION

Adsorption of indium on Si(111) produces a variety of surface reconstructions¹ that are semiconducting for coverages below one monolayer and metallic at larger coverages. At the borderline between the two regions a 4×1 phase occurs. The 4×1 unit mesh contains four indium atoms. The In atoms form two parallel zigzag chains which are separated by a zigzag silicon chain.² There is strong evidence from both experiment^{3,4} and theory⁵⁻⁷ that this structure is a *quasi*-one dimensional metallic phase. Yeom *et al.*⁸ reported that, below 120 K, the surface undergoes a phase transition to a reconstruction labeled $8\times "2"$ which is accompanied by a strong reduction of the density of states at the Fermi energy. On the basis of their angle-resolved photoemission spectra (ARPES) and scanning tunneling microscopy results, this low temperature phase was interpreted as a one-dimensional charge density wave (CDW) system driven by a Peierls transition along the rows.⁸ It was also reported that, at the transition temperature, a $4\times "2"$ phase occurs which gradually changes into a $8\times "2"$ upon further cooling.

In contrast, Kumpf *et al.* argued from surface x-ray diffraction (SXRD) results that the surface atoms change their positions at the phase transition such that a correlation perpendicular to the In chains is established.⁹ The low temperature (LT) phase transition was attributed to a modification of the In zigzag chain into a sequence of In trimers, rather than CDW formation along the chains, and the intermediate ($4\times "2"$) phase was attributed to a 8×2 phase with a high degree of " 4×2 subcell disorder." Cho *et al.*⁶ performed total energy density functional theory (DFT) calculations and proposed that, in particular, a 4×2 reconstruction was more energetically favored than the current 4×1 model. The room temperature 4×1 phase was proposed to be a thermally activated mixture of four different modifications of this 4×2 structure. Thus both the SXRD and DFT results suggest that the phase transition is a structural change. The calculated ground state band structure for the 4×1 model fits the measured bandstructure very well,^{5,6,10} but the agreement between theory and experiment for the 8×2 structure is not as

good. The atomic positions measured by Kumpf *et al.* also agree well with the 4×1 model, but again there is less convincing agreement with the 4×2 model.^{6,9} Recent ARPES (Refs. 10 and 11) and high resolution core level photoemission¹⁰ work broadly support the Peierls transition model, but with some complexities that are not understood. Adding to the difficulty in understanding this interesting system is the observation that the LT phase is extremely sensitive to surface preparation conditions, defect formation, and contamination.¹²

Summarizing, there is a broad agreement between ground state theory and experiment concerning the room temperature 4×1 phase of the surface. The conduction band states remain uncertain, due to the well known limitations of calculations within the local-density-approximation. In the case of the LT $8\times "2"$ phase, competing models for the driving force that produces the phase change, namely CDW formation,^{8,10} trimer formation,⁹ or a 4×2 reconstruction,⁶ have been proposed.

In this work two surface sensitive optical techniques, Raman spectroscopy (RS) and reflectance anisotropy spectroscopy (RAS), are used to study the phase transition. Surface steps are employed to obtain single domain growth of the low dimensional 4×1 structure on vicinal Si(111). It has been shown that such material systems are particularly suited to characterization by surface optical techniques:¹³ ordered, low-dimensional nanostructures on surfaces have the reduced symmetry that helps distinguish surface from bulk optical signals, and growth by self-assembly on surfaces with aligned steps often produces a single or dominant domain, thus reducing the problem of domain averaging of the surface optical signal. RS is used to measure vibrational modes of the surface, which strongly depend on the atomic configuration and can give, via resonance effects, information on the electronic surface states. The surface vibrational modes carry a characteristic information on surface structure which is complementary to x-ray diffraction: the bonding configuration (number, strength and direction of bonds) determines vibrational modes, rather than the precise atomic position. RAS is sensitive to electronic surface states that show up

through a different light absorption for polarizations along, and perpendicular to, the chains. The low temperature RS and RAS measurements are discussed in the framework of the competing models.

II. EXPERIMENT

Vicinal *p*-type Si(111) samples were used with a 4° offcut towards the $[11\bar{2}]$ direction. Low energy electron diffraction (LEED) confirmed that heat treatment to 1200°C , followed by rapid cooling, produced a regular step structure with 7×7 reconstructed terraces. The deposition of about 1 ML of In at a substrate temperature of 400°C to obtain a single domain 4×1 surface was monitored with RAS.¹⁴ RAS measures the difference in reflectance, at near normal incidence, of light linearly polarized in two orthogonal directions at the surface plane of a cubic material.^{15,16} The amplitude of the RAS signal is maximal if the surface is single domain (4×1). With a three-domain surface of equal statistical weight, no anisotropy is observed because of domain averaging. Deposition at 400°C was controlled by maximising the main In-related RAS feature at 2 eV. After cooling to room temperature, the size of the feature agreed well with previous studies of single domain structures.¹⁴ LEED patterns, obtained after all the optical measurements in order to minimize contamination, showed a single domain 4×1 reconstruction at room temperature. Occasionally, a very faint 7×7 pattern could still be seen, but this does not affect the spectra or discussion because the 7×7 is optically isotropic and does not show Raman modes in the energy region of interest.

After preparation the samples were transferred in vacuum to the liquid helium cooling stage where low temperature measurements were performed. The base pressure of the system was 2×10^{-10} mbar. The RAS instrument was capable of measuring from 0.8 to 6.5 eV using a CaF_2 photoelastic modulator and MgF_2 polarizers. Raman spectra were taken with a Kr^+ ion laser at 647.1 nm (1.92 eV) with an incoming and scattered polarization along the $[01\bar{1}]$ axis.

All measurements were performed either directly after sample preparation (hereafter called “fresh”), or after three days in the vacuum system (hereafter called “old”). The 4×1 to 4×2 transition is known to be prevented by small amounts of contamination.¹² Accordingly, the 4×2 phase could not be observed for old samples, the 4×1 phase being stable at all temperatures. Neither RAS nor RS at room temperature showed any significant difference between the old samples and the fresh ones, which indicated that the optical properties of the 4×1 phase can usefully be measured at low temperature with old samples. The phase transition below 120 K was verified with LEED, where the “ $\times 2$ ” streaks could be observed, but the full 8×2 LEED pattern was not obtained: the “ $\times 8$ ” superspots were not observed even at temperatures below 50 K. Since the LT-LEED measurements were performed at the end of the experiment, it could be possible that contamination prevented the formation of the 8×2 structure. However, the formation of the “ $\times 2$ ” streaks and the observation of a phase transition at temperatures consistent with previous work¹¹ make this very un-

TABLE I. Overview of surface related phonon modes, in cm^{-1} , measured for both phases at 30 K. The linewidth of a mode is given in brackets. The energy difference for the mode visible with HREELS is easily explained by a temperature related shift of the phonon modes, since our data were taken at 30 K, the HREELS data at 300 and 90 K.

RS (30 K)	4×1		4×2	
	HREELS (Ref. 17)	RS (30 K)	HREELS (Ref. 17)	
33 (20)	-	33 (3)	-	
-	-	45 (2)	-	
59 (3)	-	60 (6)	-	
65 (18)	-	-	-	
146 (50)	-	142 (12)	-	
-	-	158 (15)	-	
-	-	266 (8)	266	
-	-	415 (8)	-	
435 (10)	-	435 (13)	-	
-	-	459 (11)	-	
474 (11)	-	474 (14)	-	
493 (12)	484	493 (15)	492	

likely. It appears more reasonable that the formation of the full (8×2) structure is prevented by the high offcut angle of 40° . The average terrace width is only 45 \AA —less than two 8×2 unit cells. All reports of single domain 8×2 phases so far (if an offcut angle was reported) were on samples with offcuts of less than 2° .^{17,11} Further measurements to clarify the influence of the offcut angle are planned. The LT phase on the fresh sample will be referred to as 4×2 , in agreement with the LEED pattern, even though it is likely that some 8×2 unit cells are present but lack long range order.

III. RAMAN SPECTROSCOPY AT 30 K

The atomic configuration at the surface is different from the bulk and thus the vibrational properties of the surface are different, leading to phonon modes that are characteristic for a given surface structure.¹⁸ Surface modes were already measured for the 4×1 and 8×2 phases with high resolution electron energy loss (HREELS) at 300 and 90 K, respectively, where a mode at 60 meV (484 cm^{-1}) was observed for the 4×1 phase, and two modes at 61 meV (492 cm^{-1}) and 33 meV (266 cm^{-1}) were observed for the 8×2 .¹⁷ Surface Raman spectroscopy reproduces these modes and reveals many additional modes (see Table I). Low temperature Raman spectra of a freshly prepared 4×2 sample and of a three day old 4×1 sample are compared in Fig. 1. Strong modes at 435 and 59 cm^{-1} as well as weaker modes at 33, 65, 150 (broad), 474, and 493 cm^{-1} are observed for the 4×1 surface. The modes at 474 and 493 cm^{-1} lie on the shoulder of the bulk Si TO mode at 520 cm^{-1} . The bulk mode is not shown in Fig. 1 since it is approximately 500 times larger than the full scale in that figure. The mode at 305 cm^{-1} is the bulk Si 2TA mode which is very weak at low temperatures.¹⁹ Some structures in Fig. 1 could not be

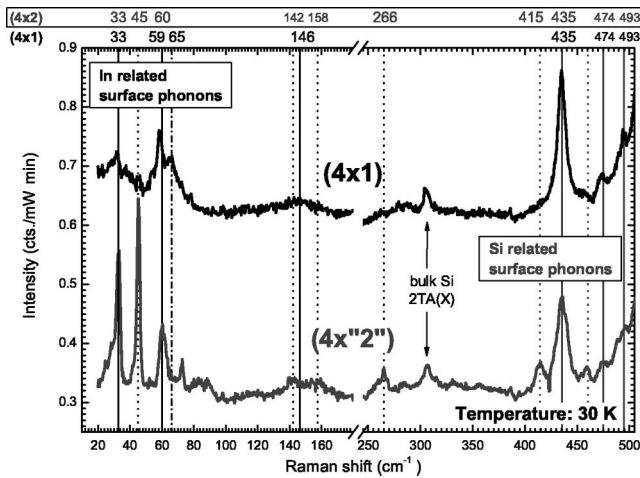


FIG. 1. Comparison of Raman spectra of the 4×1 and $4\times "2"$ phases at 30 K. The spectrum of the 4×1 phase was obtained after slight contamination of the surface which prevents the phase transition. At room temperature the 4×1 spectrum of such samples showed no significant differences from the clean spectrum. The lines mark the structures related to the 4×1 phase, additional modes for the $4\times "2"$ phase are marked with dotted lines. All measurements were taken at 647 nm and incoming and scattered polarization along $[01\bar{1}]$.

resolved on all samples, and are therefore not considered here (73 and 80–90 cm^{-1} for the $4\times "2"$ phase, as well as a structure at 230 cm^{-1}). These features will be studied more closely in additional experiments that are currently underway. On formation of the LT phase, significant differences in the spectra were observed, especially in the low frequency region. Very sharp modes appear at 33 and 45 cm^{-1} while the mode at 65 cm^{-1} cannot be distinguished anymore. At higher energies new modes are observed at 266, 415, and 459 cm^{-1} . Thus the formation of the LT phase is accompanied by the retention of the room temperature (RT) phase modes at similar intensities and frequencies (which is a remarkable observation in itself) and the appearance of new modes in the immediate vicinity of the RT phase modes.

The complete disappearance of the mode at 65 cm^{-1} confirms that no significant population of the 4×1 phase remains at these temperatures for the clean surface. Modes of a different reconstruction are being observed, with most of the vibrational modes common to both reconstructions. The atomic configurations of many of the atoms of the 4×1 and $4\times "2"$ reconstructions must therefore be very similar.

The only energy shift observed is for the mode at 59 cm^{-1} which is found at 60 cm^{-1} for the $4\times "2"$ phase. All other common modes were unchanged in energy. A maximum change of 2% in phonon energy in one common mode would suggest very little change in bond lengths on forming the $4\times "2"$ phase, in contrast to the reported changes of up to 10% in the In-In bond length measured by SXRD. The atoms involved in the observed phonon modes and the quantitative relation between position change and phonon energy are not known at present, so the question remains open whether there is a significant disagreement between the SXRD and Raman data. However, a more convincing argu-

ment against the trimer model is the fact that, while SXRD measures only interatomic distances, Raman measurements reveal bonding arrangements, so a rearrangement of In atoms into trimers should yield a different bonding configuration with a new set of significantly different modes, which was not observed at formation of the $4\times "2"$ phase.

While the Raman results make the large changes (approximately 0.5 Å) in atomic positions unlikely, the formation of the CDW would be expected to produce only small changes in the atomic positions and, due to doubling of the surface unit cell, backfolding of the phonon branches of the surface Brillouin Zone (SBZ). As phonon branches normally show dispersion, the backfolding can lead to the appearance of new phonon modes at the center of the SBZ probed by RS, with the original mode being retained at an unchanged energy. The modes at 33 and 45 and 415 and 435 cm^{-1} , together with the separation of the 150 cm^{-1} mode into two, lend themselves to this interpretation. In addition, such a zone folding could generate an optical mode from an acoustic mode in regions where there was no observable mode prior to folding: the mode at 266 cm^{-1} could arise in this way. Such qualitative arguments provide an elegant explanation of the unusual phonon mode structure observed and lend weight to the CDW model of the LT phase.^{8,10} While the CDW mechanism can not directly be proven, our RS results demonstrate clearly that a restructuring yielding a larger surface unit mesh (as seen with diffraction techniques as well) takes place without a substantial modification of the bonding configuration in the surface layer.

The large increase in the Raman intensity of the 33 cm^{-1} mode on formation of the $4\times "2"$ phase may be a resonance effect, since the laser photon energy (1.92 eV) corresponds exactly to an electronic transition within the surface band structure that changes on formation of the phase, as observed by RAS (see below). The Raman scattering intensity for vibrational modes coupled to surface states can be strongly enhanced if the incident laser light is resonant to a transition within the surface band structure.^{20,18}

No calculations of surface phonon modes for the Si(111)-(4 $\times 1$)In surface are available, but some general observations may be made. The mode at 435 cm^{-1} is close to those calculated for Si dimer chains on the Si(111)-(2 $\times 1$) surface (435 and 412 cm^{-1}).²¹ Since the Si(111)-(4 $\times 1$)In structure has a similar Si chain, isolated from the In chains,^{2,6} it is likely that such a vibrational mode could exist. In the low frequency region, below 150 cm^{-1} , vibrational modes mainly related to In-In bonds are expected, since the In atoms are heavier than the Si atoms and In-In bonding is generally weaker than Si-Si bonding. For example, the highest bulk vibrational mode of indium is a longitudinal acoustic mode at 114 cm^{-1} , with transverse acoustic modes at 25 and 34 cm^{-1} .²² Calculation of the surface phonon modes of this system is clearly needed to make further progress. Such calculations are the only reliable way to match changes in atomic positions to the observed changes in the Raman spectra. This should be feasible as similar calculations have already been performed for the Si(111)-($\sqrt{3}\times\sqrt{3}$)In reconstruction.²³

Concluding this section, the Raman data for the LT phase

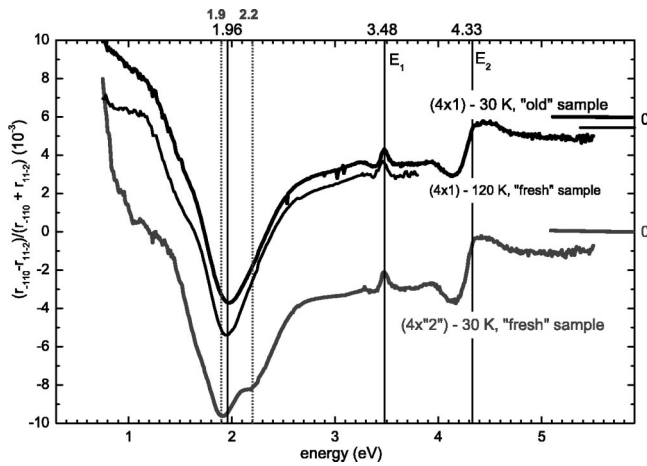


FIG. 2. Comparison of RAS spectra of the 4×1 and $4 \times '2'$ phases at 30 K. The spectrum of the 4×1 phase was obtained after slight contamination of the surface in order to suppress the phase transition. The clean spectrum at 120 K is shown for comparison.

can be elegantly explained by the backfolding of surface bands within the SBZ on CDW formation.¹⁰ Alternative models involving significant changes in atomic positions or rearrangement of atomic bonds are not likely because of the presence of many of the surface Raman modes of the 4×1 phase in the spectrum of the $4 \times '2'$ phase at the same energy.

IV. REFLECTANCE ANISOTROPY SPECTROSCOPY AT 30 K

The geometry of the RAS experiment was chosen to measure the difference in reflectance along, and perpendicular to, the In chains. RAS of the 4×1 surface (Fig. 2) displays a dominant reflectivity perpendicular to the chains at 2.0 eV, and thus a minimum in the spectra, which has been attributed to In-Si backbonds in earlier studies by Pedreschi *et al.*¹⁴ The extended energy range of our spectrometer reveals a dominant reflectivity along the chains in the near infrared regime below 1 eV. Spectra of the $4 \times '2'$ phase show a splitting of the feature around 2-eV and a substantial increase in anisotropy in the near IR. The splitting of the 2 eV peak into one at 1.9 eV and one at 2.2 eV cannot be explained as a temperature-induced sharpening of the original 2-eV peak, since the overall width of the structure is much larger for the LT phase. There is a small difference in the infrared region between the clean spectrum at 120 K (Fig. 2) and the slightly contaminated spectrum at 30 K but elsewhere the spectra can be seen to be almost identical.

In previous RAS work²⁴ on the metallic 4×1 phase, we suggested that the large, positive anisotropy in the near infrared region was consistent with a Drude-like $\epsilon_{\perp 10}$ response. The $4 \times '2'$ phase is reported to be non or less metallic,^{8,10,11} but a larger anisotropy is measured at the same temperature, in contrast to a simple Drude-like response. Differences in the band structure of the two phases are, however, confined to a region very close to the Fermi level.¹⁰ It follows that the density of localized states close to the Fermi level may well

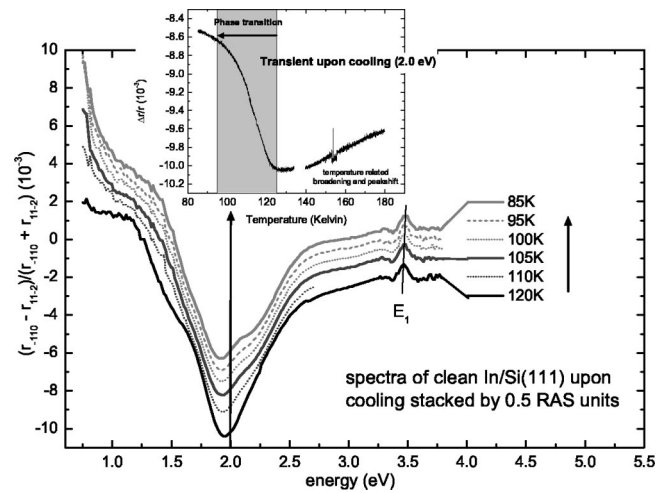


FIG. 3. RAS spectra, displaced by 0.5×10^{-3} , at temperatures around the surface phase transition. The splitting of the negative structure around 2 eV can be seen, as well as an increase of the anisotropy below 0.9 eV. The inset shows the RAS transient measured at 2.0 eV. The magnitude of the anisotropy decreases at the phase transition due to splitting of the RAS minimum around 2 eV.

increase as the density of itinerant states at the Fermi level decreases on formation of the $4 \times '2'$ phase, thus producing the increase in reflectivity observed. By extending the RAS measurement further into the infrared it should be possible to distinguish Drude-like and localized state behavior.

Using the surface band structure to interpret the RAS spectra in more detail is difficult because the position of the conduction band states remains uncertain, due to the well known limitations of local-density-approximation calculations, and because small differences in the oscillator strength of electronic transitions in either or both of the orthogonal directions in the surface can produce a significant change in the spectrum. However, it is tempting to link the enhanced Raman intensity of the $4 \times '2'$ phase (Fig. 1) with the splitting of the deep RAS minimum, which shifts the position of the minimum from 1.96 to 1.90 eV and thus much closer to resonance with the Raman excitation energy at 1.92 eV. The backfolding of the surface electronic bands in the SBZ induced by CDW formation would also provide an explanation for the RAS observation. An excited state dispersing by 0.3 eV could, after backfolding, create two states with an energy difference sufficient to explain the splitting of the 2 eV signal. Since all but one of the ground state surface bands in this energy region disperse significantly and also cross the Fermi level,^{3,5-8,10,11} backfolding could also lead to empty surface states contributing to the new structure appearing below 1 eV. A more detailed interpretation awaits specific calculation of the optical anisotropy.

V. REAL TIME MONITORING OF THE PHASE TRANSITION (VARIABLE T)

The development of the RAS spectra in the temperature region between 120 to 80 K is shown in Fig. 3. In order to estimate the transition temperature, the RAS transient at 2.0 eV was measured. Since the minimum of the RAS spectrum

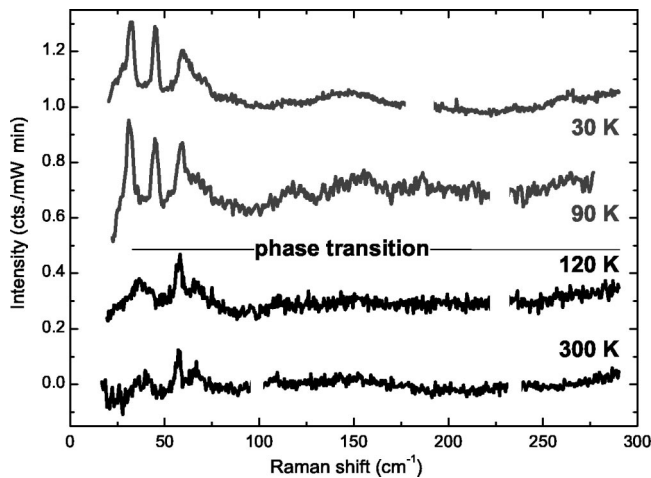


FIG. 4. Development of the Raman spectrum upon cooling. The change of the mode around 35 cm^{-1} into two modes at 33 and 45 cm^{-1} , accompanied by an intensity increase, can be seen. The mode at 59 cm^{-1} remains unchanged.

of the 4×1 reconstruction is at 1.96 eV (at 30 K) the magnitude of the (negative) signal at 2.0 eV is expected to increase on cooling due to the blueshift and sharpening of RAS structures. This effect can indeed be observed between 300 and 130 K . Below that temperature, the magnitude of the signal decreases due to the development of the $4 \times "2"$ double peak structure at 1.9 and 2.2 eV . The transition shows a sharp onset at 125 K , and 90% of the signal change is completed by 95 K . This 30-K range contrasts with a range of 10 K reported in previous work¹¹ and may be associated with the small terrace width of the 4° offcut. However, our RAS system illuminates the whole of the sample and thus a broadening of the transition due to a temperature gradient across the sample is the more likely explanation. The presence of a phase transition at this temperature is good evidence that the same general reconstruction is occurring, even though the $" \times 8 "$ superspots are not observed. Below 90 K the change in the signal cannot be easily assigned to changes in the reconstruction, since the temperature-related sharpening of the RAS structures can have a similar effect.

Similar temperature dependent RS measurements are shown in Fig. 4. The transition between the 4×1 and $4 \times "2"$ phases, discussed above, occurs in the temperature region between 120 and 90 K . The measurements were performed with a one day old sample and so the spectrum at 30 K is a linear combination of 4×1 and $4 \times "2"$ phases. Hence the modes at 33 and 45 cm^{-1} are not as pronounced as in Fig. 1, and the mode at 65 cm^{-1} is still visible.

The similarity of the low temperature optical spectra of an old sample with the spectrum of a clean 4×1 phase above the transition temperature (see Fig. 2) challenges the 4×2 superposition model of Cho *et al.* If the 4×1 phase were a thermally activated mixture of four different 4×2 reconstructions, then it should not be observed below the transition temperature, and the presence of small amounts of contamination would be expected to lock the system into a 4×2

phase. In contrast, we have shown that a small contamination results in low temperature spectra with lineshapes very similar to spectra of the 4×1 phase above the transition temperature.

VI. CONCLUSIONS

We have shown that the phase transition of the $\text{Si}(111)\text{-}(4 \times 1)\text{In}$ surface below 120 K can be monitored with optical techniques such as Raman spectroscopy and reflectance anisotropy spectroscopy. RS shows that the 4×1 and $4 \times "2"$ surface phases possess distinct, but similar, sets of vibrational modes. The surface Raman spectrum shows a sharpening and splitting of phonon lines upon a transition into the $4 \times "2"$ surface phase. RAS of the $4 \times "2"$ phase also shows significant differences compared with the 4×1 phase: the deep minimum at 2 eV splits, and an increase in intensity is observed below 0.9 eV . Using RS and RAS the 4×1 phase was shown to be stable (i.e., the $4 \times "2"$ phase formation is suppressed) to low temperatures in the presence of slight contamination by residual gases in the ultrahigh vacuum environment. LT measurements of the 4×1 phase, obtained from slightly contaminated surfaces, were presented to allow easier comparison with the LT $4 \times "2"$ phase. The RT spectra of these lightly contaminated surfaces were the same as those from fresh samples.

The assignment of the observed features is limited by the absence of phonon dispersion and optical anisotropy calculations. However, the unchanged energy of the common phonon modes of the LT phase, together with the increase in the number of modes observed, render the trimer formation model⁹ of the $4 \times "2"$ phase unlikely. Within the model of the 4×1 phase as a superposition of almost degenerate 4×2 reconstructions,⁶ it is not obvious how slight contamination can prevent freezing into a single 4×2 phase at low temperatures. The sensitivity of the $4 \times "2"$ phase to contamination and the observed surface Raman spectrum is most straightforwardly explained by the formation of a charge density wave and the folding of the surface Brillouin zone.^{8,10}

In contrast to the Raman results there is a difference in the RAS spectra of the slightly contaminated and clean 4×1 surfaces. It is interesting to speculate that the RAS spectra at low energies may be revealing the small changes in the surface electronic states that prevent or drive the CDW formation.

A more detailed interpretation awaits the calculation of the optical anisotropy and the surface vibrational modes. In addition, experimental studies of polarization dependence and resonance effects in the Raman spectra are currently underway and are expected to reveal more information concerning the symmetry and origin of the vibrational modes.

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- ¹J. Kraft, M. G. Ramsey, and F. P. Netzer, Phys. Rev. B **55**, 5384 (1997).
- ²O. Bunk, G. Falkenberg, J. H. Zeysing, L. Lottermoser, R. L. Johnson, M. Nielsen, F. Berg-Rasmussen, J. Baker, and R. Feidenhans'l, Phys. Rev. B **59**, 12 228 (1999).
- ³T. Abukawa, M. Sasaki, F. Hisamatsu, T. Goto, T. Kinoshita, A. Kakizaki, and S. Kono, Surf. Sci. **325**, 33 (1995).
- ⁴I. G. Hill and A. B. McLean, Phys. Rev. Lett. **82**, 2155 (1999).
- ⁵J. Nakamura, S. Watanabe, and M. Aono, Phys. Rev. B **63**, 193307 (2001).
- ⁶J.-H. Cho, D.-H. Oh, K. S. Kim, and L. Kleinman, Phys. Rev. B **64**, 235302 (2001).
- ⁷R. H. Miwa and G. P. Srivastava, Surf. Sci. **473**, 123 (2001).
- ⁸H. W. Yeom *et al.*, Phys. Rev. Lett. **82**, 4898 (1999).
- ⁹C. Kumpf, O. Bunk, J. H. Zeysing, Y. Su, M. Nielsen, R. L. Johnson, R. Feidenhans'l, and K. Bechgaard, Phys. Rev. Lett. **85**, 4916 (2000).
- ¹⁰H. W. Yeom, K. Horikoshi, H. M. Zhang, K. Ono, and R. I. G. Uhrberg, Phys. Rev. B **65**, 241307(R) (2002).
- ¹¹O. Gallus, T. Pillo, M. Hengsberger, P. Segovia, and Y. Baer, Eur. Phys. J. B **20**, 313 (2001).
- ¹²S. V. Ryjkov, T. Nagao, V. G. Lifshits, and S. Hasegawa, Surf. Sci. **488**, 15 (2001).
- ¹³J. F. McGilp, Phys. Status Solidi A **188**, 1361 (2001).
- ¹⁴F. Pedreschi, J. D. O'Mahony, P. Weightman, and J. R. Power, Appl. Phys. Lett. **73**, 2152 (1998).
- ¹⁵D. E. Aspnes and A. A. Studna, Phys. Rev. Lett. **17**, 1956 (1985).
- ¹⁶V. L. Berkovits, I. V. Makarenko, T. A. Minashvili, and V. I. Safarov, Solid State Commun. **56**, 449 (1985).
- ¹⁷K. Sakamoto, H. Ashima, H. W. Yeom, and W. Uchida, Phys. Rev. B **62**, 9923 (2000).
- ¹⁸*Light Scattering in Solids VIII: Raman Scattering from Surface Phonons*, edited by M. Cardona and G. Güntherodt (Springer-Verlag, Berlin, 1999).
- ¹⁹P. A. Temple and C. E. Hathaway, Phys. Rev. B **7**, 3685 (1973).
- ²⁰P. V. Santos, N. Esser, M. Cardona, W. G. Schmidt, and F. Bechstedt, Phys. Rev. B **52**, 12 158 (1995).
- ²¹J. Fritsch and P. Pavone, Surf. Sci. **344**, 159 (1995).
- ²²A. S. Bakulin, A. W. Overhauser, H. Kaiser, S. A. Werner, J. A. Fernandez-Baca, and H. G. Smith, Phys. Rev. B **63**, 052301 (2001).
- ²³J. Fritsch, J. Phys.: Condens. Matter **13**, 7611 (2001).
- ²⁴K. Fleischer, S. Chandola, N. Esser, W. Richter, and J. F. McGilp, Phys. Status Solidi A **188**, 1411 (2001).