PHYSICAL REVIEW B **66**, 035325 (2002)

Quantized valence states of the Pb/Si(111) mosaic phase

B. Ressel,[1,2] J. Slezák,[2,*] K. C. Prince,[1] and V. Cháb[2]
[1]*Sincrotrone Trieste, Strada Statale 14, km 163.5, 34012 Basovizza, Trieste, Italy*
[2]*Institute of Physics of the Academy of Science of the Czech Republic, Cukrovarnická 10, 16253 Prague 6, Czech Republic*

(Received 13 February 2002; published 24 July 2002)

The Pb/Si(111)-($\sqrt{3}\times\sqrt{3}$)$R30°$ mosaic phase, whose surface consists of $\approx\frac{1}{6}$ ML of Pb and $\frac{1}{6}$ ML of Si, has been studied by scanning tunneling spectroscopy. The top of the valence band consists of Pb $6p_z$ derived states, which are quantized into a series of about four equally spaced, narrow peaks. The sharpness and regular ordering of these states is unexpected considering that the surface is chemically disordered, with no long-range order. The existence of these states is attributed to correlations in the short-range order, and is consistent with published calculations of one-dimensional systems.

DOI: 10.1103/PhysRevB.66.035325 PACS number(s): 73.20.At, 68.37.Ef, 68.35.−p, 73.20.Hb

Since lead and silicon do not form bulk alloys, the Pb/Si(111) system first attracted considerable interest as a prototype for an ideal, unreacted Schottky barrier suitable for testing theories of diode formation.[1–4] However it was soon discovered that the adsorption system is more complex and that in fact it forms two-dimensional surface alloys, in particular, on the most commonly studied (111) surface. Furthermore, the closely related Sn/Si(111), Sn/Ge(111), and Pb/Ge(111) surfaces have recently aroused considerable controversy with the discovery that phase transitions on these surfaces are driven by charge-density waves.[5–8] These surfaces all form ($\sqrt{3}\times\sqrt{3}$)$R30°$ structures with a metal coverage of $\frac{1}{3}$ ML that undergo a transition to (3×3) at low temperature. Others have suggested that the phase transitions are in fact of the order-disorder type,[9] but this counterclaim was not supported by x-ray standing-wave measurements[10] or photoemission.[11] Bunk *et al.* showed that the transition was clearly not of the order-disorder kind, and suggested that it was Jahn-Teller-like. It has recently been shown that similar transitions can be observed in the Pb/Si(111) system by scanning tunnel microscopy (STM) and by reflection high-energy electron diffraction (RHEED).[12,13]

While this work has focused on the ($\sqrt{3}\times\sqrt{3}$)$R30°$ phase at $\frac{1}{3}$ ML of metal coverage ($1\ \mathrm{ML}=7.83\times10^{14}$ atoms/cm^2, the number of silicon atoms in an ideally terminated surface), at a coverage of about $\frac{1}{6}$ ML there appears another ($\sqrt{3}\times\sqrt{3}$)$R30°$ structure known as the mosaic phase, or alternatively as the ($\sqrt{3}\times\sqrt{3}$)$R30°$-γ phase.[14] From STM studies[15] the currently accepted model of the structure is that it consists of Pb and Si atoms in T_4 sites on an ideally terminated Si(111) substrate. The surface Si and Pb atoms are on lattice sites but are rather disordered, as no long-range chemical order is present. Nevertheless it is not a completely disordered lattice gas as the Pb atoms form chains of varying length. These chains are short, being up to about 8 or 12 unit cells in length, and considerably branched. The surface consists of a solid solution with a total coverage of about one-third of a monolayer; a typical composition of the surface atoms is 54% Pb, 43% Si, and 3% vacancies.

The electronic structure of disordered systems is a subject of intense current interest. Some time ago, Anderson showed that the electronic states of fully disordered systems in one and two dimensions are localized,[16] and since then further studies have demonstrated both rigorously true cases and exceptions.[17–23] For the case of correlated disorder, where the disorder is not complete, extended states may exist, and the ramifications for electronic and phonon bands as well as transport phenomena have been studied. The concepts have wide applications from the atomic scale of partly disordered alloys to superlattices and superconductors.

Previously the morphology of the mosaic phase has been studied by STM (Refs. 24 and 25), and electronic structure measurements consist of scanning tunneling spectra (STS),[25] valence level, and core-level photoemission.[14] The latter authors observed three surface induced bands, labeled $S1$ to $S3$, and concluded that the surface was semiconducting. Both groups reported Si core-level spectra in which one of the peaks was shifted to lower binding energy by about 0.53 eV. Karlsson *et al.* assigned a peak at 0.67 eV higher binding energy to the surface Si atoms, and concluded that there was strong charge transfer to the Pb atom. Recently the electronic structure of the corresponding mosaic phase on Ge has been calculated and compared with Pb/Si by Stumpf, Carpinelli, and Weitering,[26] and they concluded that there was negligible charge transfer in the surface plane, although other authors continue to discuss charge transfer. The calculations simulated well the core-level shifts of the substrate atoms, but for the surface shift they obtained the opposite sign to that measured (−0.43 eV instead of +0.67 eV.)

The discussion of charge transfer is partly semantic as sometimes it signifies the charge transfer to or from the dangling bond of the surface atoms, and sometimes the total valence charge. The surface energy is minimized by forming a ($\sqrt{3}\times\sqrt{3}$)$R30°$ structure so that each of the three Si atoms of the (1×1) surface with a dangling bond are replaced by one atom, either an Si or a Pb atom; the problem then remains of how to minimize the energy of these atoms. Removing the charge from the Si dangling-bond orbital and placing it in the highest unoccupied Pb orbital appears to be one way. The charge distribution of other, more tightly bound orbitals can then change to minimize large overall differences in charge.

As part of a general study of the Pb/Si system, we have performed STS measurements of the mosaic phase and observed surprising electronic structure, namely, an unusual quantization of the states at the top of the valence band.

0163-1829/2002/66(3)/035325(5)/$20.00

Samples were cut from a Si(111) wafer with a resistivity of 1–10 Ω cm and degassed overnight at 600 °C. Heating was achieved by passing direct current through the sample. A clean Si(111)-(7×7) reconstructed surface was obtained by flashing the sample several times to 1200 °C followed by slow cooling from 850 °C to room temperature (RT) at a rate of approximately 30 °C per minute. Lead was evaporated from a water-cooled source heated by electron bombardment (EFM3 Focus, Omicron Ltd.). The STM used was a commercial, variable-temperature Omicron instrument with a base pressure in the experimental chamber of 5×10^{-11} mbars and a maximum pressure during Pb deposition of 1×10^{-10} mbars. The electrochemically etched tungsten tip was cleaned in vacuum by annealing for 3 min, and sharpened by pulsing to 10 V while scanning a trial sample. The images and spectra were acquired at room temperature.

Images of the mosaic phase are shown in Figs. 1(a) and 1(b), together with a schematic model. It has a labyrinthine form like a maze, and is characterized by short Pb-Si-Pb chains of from 2 to about 12 Pb atoms, which branch at angles of 60° or 120°. Sometimes they form hexagonal motifs, which may be more or less complete. The Pb-Pb distance is 6.65 Å along the chains and 11.5 Å between adjacent chains. This structure was produced by annealing an initial coverage of about 1.5 ML deposited at RT to approximately 350 °C for 3 min.[15] At this temperature partial desorption of the Pb occurs, as well as ordering. In spite of many trials with varying times and temperatures of annealing, we have not succeeded in producing longer chains. Both the Pb and Si atoms are on lattice sites, but the structure contains considerable disorder, and is without long-range order.

As reported previously,[24] for tunneling into empty states (positive sample bias) both Si and Pb atoms are imaged with nearly equal contrast. Depending on the bias voltage, some contrast can be occasionally seen. This is not believed to be topographical contrast as it practically disappears at lower voltage. There are also objects on the surface, which are dark for both positive and negative voltage and these are interpreted as vacancies.

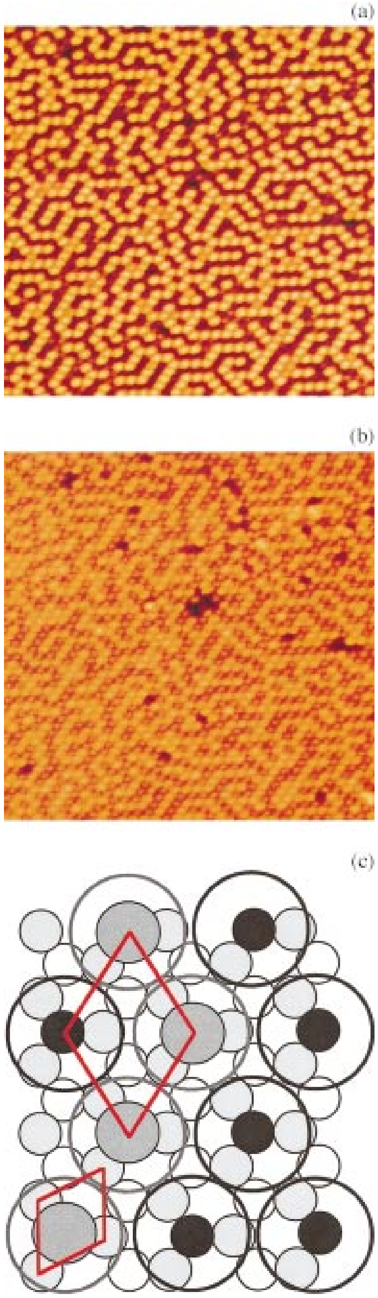

FIG. 1. (Color) (a) Filled state image of the mosaic phase. Field of view 200 Å. Sample bias=−1.9 V, tunneling current 0.6 nA. (b) Empty state image of the mosaic phase. Same field of view. Sample bias=+1.9 V, tunneling current 0.6 nA. (c) Schematic model of the structure, reproducing the STM image of the filled states. The medium-sized dotted circles represent Pb, the filled circles represent Si atoms in the top layer, the shaded circles represent second layer Si, and the small unfilled circles denote third layer Si atoms. The sizes of these reflect the covalent radii of Pb and Si atoms. The largest unfilled black and gray circles correspond to the size of atoms observed in STM images. The larger and smaller rhombi represent the $(\sqrt{3}\times\sqrt{3})R30°$ and the (1×1) unit cells, respectively.

In the filled state images the Pb atoms are bright, indicating that at the top of the valence band there is a higher density of charge on the metal, although it does not provide information about the charge density at higher binding energies. As noted above, the issue of Pb-Si charge transfer is controversial[25,26] but if it is present here, it suggests a simple explanation for the structure of the mosaic phase: it appears to be a realization of the antiferromagnetic Ising model on a triangular surface. The up and down spins of an Ising model correspond to positive and negative charges on Si and Pb atoms, or simply to the atoms. This phase is frustrated and does not have a unique low-temperature structure[27]—it is degenerate, and may consist of chains of similarly charged atoms, or honeycomb structures, or a mixture of both, and still be in its ground state. The rule for the formation of a ground state is that the average atom is coordinated by two similar nearest neighbors and four of opposite spin/charge. The structure is degenerate because it can consist of many different configurations. In addition, it can be shown analytically that the antiferromagnetic Ising model does not undergo a phase transition. We have verified experimentally with low-energy electron diffraction from 130 K and with STM from 70 K up to the desorption temperature of Pb that the present structure does not in fact undergo a phase transi-

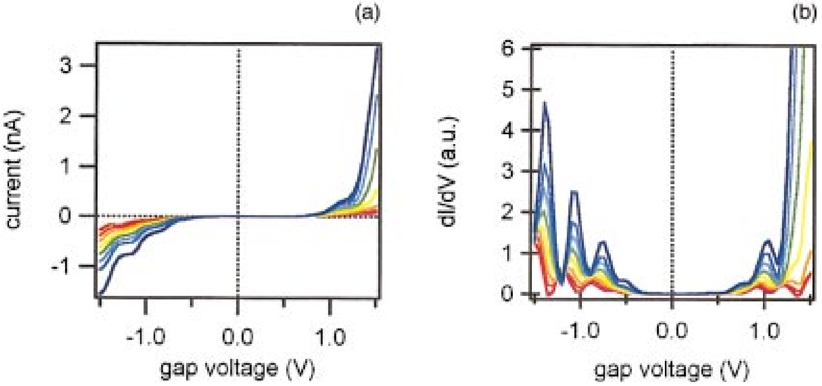

FIG. 2. (Color) (a) Scanning tunneling spectra of current versus voltage at various tip-surface distances. Height determined at a tunneling current of 0.3 nA and 1.9 V in STM topography. Lowest current curve: voltage 1.9 V [≈9 Å from the surface (Ref. 20)]. Highest current curve: voltage 1.2 V [≈7 Å from the surface (Ref. 20)]. The spectra are taken in steps of 0.1 V. (b) Derivative with respect to voltage of the same data (dI/dV), which reflects the density of states near the Fermi level (Ref. 20).

tion. This behavior is in strong contrast with the higher metal coverage $(\sqrt{3}\times\sqrt{3})R30°$ systems discussed above. The Coulomb force is not a nearest-neighbor interaction as assumed in an Ising model, but a dipolar or the screened Coulomb interaction may approximate it sufficiently well. Indeed any sixfold symmetric, short-range attractive interactions between Pb and Si, which are also repulsive for Pb-Pb and Si-Si, will place the system in this universality class.

Thus this system exhibits correlated or short-range order. For a stoichiometric system in its ground state, the two-point correlation function of a Pb atom gives a value for two Pb atoms in the first coordination shell, rather than the statistical value of 3. The present sample is slightly nonstoichiometric, so a random system would have 3.2 Pb atoms in the first shell. The measured value of 2.36 indicates strong short-range correlation.

Figure 2 shows a series of scanning tunneling spectra as a function of tip-surface distance. A topographic image was taken at the appropriate voltage and current of 0.3 nA; the tip was stopped at regular intervals and a spectrum taken at fixed height at a point on the sample. The voltage and current were returned to their original values and the scan continued. For each image, 1600 spectra were averaged to yield the spectra shown. Finally the tip-surface distance was estimated using the calibration of Stroscio, Feenstra, and Fein.[28]

These spectra show much more structure than those of Gomez-Rodriguez, Veuillen, and Cinti[24] who observed only one or two broad peaks in a 2-V range above or below the Fermi level. We attribute this inconsistency to a difference in sample quality (the average linear chain length of the present sample is greater, indicating better quality) and/or better spectroscopic resolution.

Four clear peaks in the density of occupied states are evident, linearly spaced at intervals of 300 meV and with a width of about 250 meV. It is well known that the derivative of the I-V curve is related to the density of states in the valence band.[28] Usually the normalized derivative $(dI/dV)\times(I/V)$ is used, but for the sake of clarity we plot the simple derivative, which shows more clearly the variation of the peak energy with tip voltage. In the unoccupied states, at least two peaks are visible (the divergence at high positive voltage is not relevant here). The surfaces giving the sharpest spectra are semiconducting with a gap of 0.8 eV determined by the zero current region of the curve, consistent with the behavior observed by Karlsson *et al.*[25] There is some apparent dispersion as the distance from the tip to the surface changes, and the whole spectrum in both the occupied and empty states moves rigidly. This shift is interpreted as a high-field effect and eliminates the possibility that these states are due to a tip-surface artifact, such as standing waves.[29]

For less ordered surfaces with slightly different stoichiometry and generally shorter chains, the gap appeared to be smaller and the states were less sharp. This is in line with what is expected for disordering, namely, that the valence states are smeared out. However these discrete structures were not observed on well-ordered surfaces without the mosaic structure, for example, Si(111)-Pb-(7×7), Si(111)-Pb-$(\sqrt{3}\times\sqrt{3})R30°$, Si(111)-Pb-(1×1), and so forth. They are thus characteristic of the mosaic structure.

The peaks are surprisingly sharp in view of the considerable disorder of the surface, and evidently do not hybridize with the bulk. We assign them to Pb $6p$–Si *sp* hybrid states and to determine their origin we took the spectra shown in

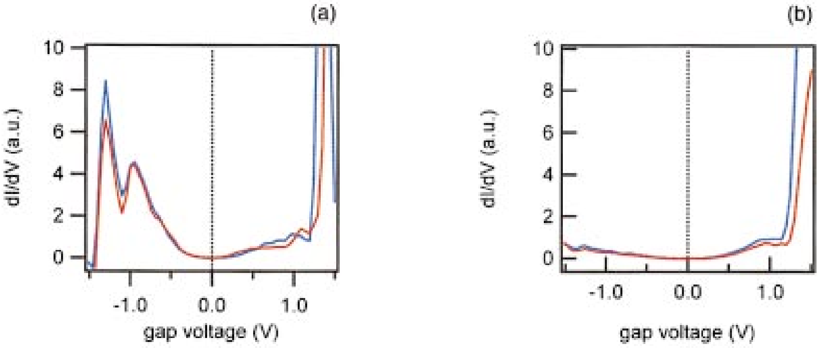

FIG. 3. (Color) (a) Element specific STS signal from Pb atoms. Height determined at a tunneling current of 0.6 nA and 1.3 V in STM topography. Two peaks are clearly resolved and a third is visible as a shoulder at ~0.6 V. The spectrum corresponds most closely to the upper curve in Fig. 2(b), with a slight offset on the *x* axis (~100 meV). (b) STS signal from Si atoms, same conditions.

Fig. 3. These are STS spectra taken from individual atoms in an image, and have a much poorer signal-to-noise ratio than those of Fig. 2, which are integrated over many more points. Nevertheless two clear peaks and a shoulder are visible in the spectra from Pb atoms with the same spacing, while only a hint is present in the Si spectra. Furthermore, the signal from Pb is about an order of magnitude stronger than from Si for the same tip-sample distance. We conclude that the states have mainly Pb $6p$ character. Conversely the empty state signal from Si is stronger than that of Pb, and they are assigned to empty Si *sp* states derived from the dangling bonds that have been emptied.

In photoemission[25] three surface-state bands are observed at 0.3, 1.5, and 1.9 eV below the Fermi level at the $\bar{\Gamma}$ point, and the present states are evidently related. However the energy spacing is quite different from the photoemission surface states; the STS peaks could fit within the envelope of the first photoemission state. Stumpf, Carpinelli, and Weitering[26] have calculated that the upper band, $S1$, is substantially Pb $6p_z$ using a band-structure formalism. This is confirmed by the spatially resolved spectra, Fig. 3, but the calculation does not predict the quantization observed here. This is not surprising since it assumed a periodic structure whereas a key property of the real structure is its lack of long-range order. The present data confirm the model of charge transfer from the dangling bond of Si to that of Pb, with a consequent depletion of charge on Si at the top of the valence band and a higher density of empty states at the bottom of the conduction band. It is remarkable that although the chains are of mixed length and shape, they do not smear out or form a band with an average spectral density. We believe that this is a consequence of the correlated disorder of the system. We are not aware of any calculations of the density of states of the frustrated Ising model on a triangular lattice, but several calculations have been performed for one-dimensional chains with correlated disorder. Heinrichs[17] has shown that for a disordered linear chain, introduction of some local order (trimer model) causes the appearance of six delocalized states, four of which are linearly spaced. Similarly Arzhnikov, Bagrets, and Bagrets[21] have performed analytical and numerical calculations for *AB* alloy chains with correlated disorder. For attractive *AB* interactions and limited correlation they obtain three or four roughly equally spaced bands, depending on the values of the parameters. This is of course only a guide to expected behavior in two dimensions, but it strongly suggests that systems with correlated disorder can possess discrete bands. We note that in other low-dimensional systems, linear band spacing can occur. Eggert, Mattsson, and Kinaret[30] have shown that in one-dimensional systems new phenomena arise, and that the energy levels are linearly spaced, for example, as observed here.

These states resemble quantum well states that are observed on surfaces, such as those reported by Yokoyama and Takayanagi.[31] They observed quantum confinement between long dimer rows of Al on Si(001) 15–85 Å apart, and were able to observe up to five states with a spacing of 150–300 meV. However there are some important differences: the confinement is rather tighter in the present case, with a distance of 11.5 Å between adjacent chains of Pb atoms. Above all, for Al/Si(001) the chains were long and well ordered whereas in the present case they are short and branched. We conclude that to observe one-dimensional quantum confinement, long-range order is not essential.

As noted above, the work of Anderson showed that for a completely disordered two-dimensional system the states are exponentially localized and thus an infinite number of states exists in an extended system with a continuous density of states. This is not the case here as a finite number of discrete bands exists. The system is, therefore, a physical realization of correlated disorder, where the rules for the local order are those of the frustrated Ising model on a triangular lattice.

The authors acknowledge support from the Grant Agency of Czech Republic (Grants No. 202/99/P001 and No. 202/98/K002) and the European Union under Contract No. ERB IC CT 970700.

---

[*] Present address: SCG Czech Design Center, ON Semiconductor, Nemcove 1720, Roznov pod Radhostem, Czech Republic.

[1] D. R. Heslinga, H. H. Weitering, D. P. van der Werf, T. P. Klapwijk, and T. Hibma, Phys. Rev. Lett. **64**, 1589 (1990).

[2] G. Le Lay and H. Hricovini, Phys. Rev. Lett. **64**, 807 (1990).

[3] H. H. Weitering, A. R. H. F. Ettema, and T. Hibma, Phys. Rev. B **45**, 599 (1992).

[4] D. Tang, H. E. Elsayed-Ali, J. Wendelken, and J. Xu, Phys. Rev. B **52**, 1481 (1995).

[5] J. M. Carpinelli, H. H. Weitering, E. W. Plummer, and R. Stumpf, Nature (London) **381**, 398 (1996).

[6] J. M. Carpinelli, H. H. Weitering, M. Bartkowiak, R. Stumpf, and E. W. Plummer, Phys. Rev. Lett. **79**, 2859 (1997); L. Ottaviano, A. V. Melechko, S. Santucci, and E. W. Plummer, *ibid.* **86**, 1809 (2001).

[7] A. V. Melechko, J. Braun, H. H. Weitering, and E. W. Plummer, Phys. Rev. B **61**, 2235 (2000).

[8] J. Avila, A. Mascaraque, E. G. Michel, M. C. Asensio, G. LeLay, J. Ortega, R. Pérez, and F. Flores, Phys. Rev. Lett. **82**, 442 (1999).

[9] A. Goldoni, C. Cepek, and S. Modesti, Phys. Rev. B **55**, 4109 (1997).

[10] O. Bunk, J. H. Zeysing, G. Falkenberg, R. L. Johnson, M. Nielsen, M. M. Nielsen, and R. Feidenhans'l, Phys. Rev. Lett. **83**, 2226 (1999).

[11] T. E. Kidd, T. Miller, and T.-C. Chiang, Phys. Rev. Lett. **83**, 2789 (1999); T. E. Kidd, T. Miller, M. Y. Chou, and T. C. Chiang, *ibid.* **85**, 3684 (2000).

[12] J. Slezák, P. Mutombo, and V. Cháb, Phys. Rev. B **60**, 13 328 (1999).

[13] K. Horikoshi, X. Tong, T. Nagao, and S. Hasegawa, Phys. Rev. B **60**, 13 287 (1999).

[14] J. A. Carlisle, T. Miller, and T. C. Chiang, Phys. Rev. B **45**, 3400 (1992).

[15] E. Ganz, I.-S. Hwang, F. Xiong, S. K. Theiss, and J. Golovchenko, Surf. Sci. **257**, 259 (1991).

[16] P. W. Anderson, Phys. Rev. **109**, 1492 (1958); P. W. Anderson, Phys. Rev. B **23**, 4828 (1981).

[17] J. Heinrichs, Phys. Rev. B **51**, 5699 (1995).

[18] U. Kuhl and H.-J. Stöckmann, Phys. Rev. B **63**, 132201 (2001).

[19] F. M. Izrailev, A. A. Krokhin, and S. E. Ulloa, Phys. Rev. B **63**, 041102 (2001).

[20] A. Ghosh and S. N. Karmakar, Phys. Rev. B **61**, 1051 (2000).

[21] A. K. Arzhnikov, A. A. Bagrets, and D. A. Bagrets, Phys. Rev. B **60**, 7178 (1999).

[22] J. A. Ketoja and I. I. Satija, Phys. Rev. B **59**, 9174 (1999).

[23] V. Bellani, E. Diez, R. Hey, L. Toni, L. Tarricone, G. B. Parravicini, F. Dominguez-Adame, and R. Gomez-Alcala, Phys. Rev. Lett. **82**, 2159 (1999).

[24] J. M. Gomez-Rodriguez, J.-Y. Veuillen, and R. C. Cinti, Surf. Sci. **377–379**, 45 (1997).

[25] C. J. Karlsson, E. Landemark, Y.-C. Chao, and R. I. G. Uhrberg, Phys. Rev. B **45**, 6321 (1992).

[26] R. R. Stumpf, J. M. Carpinelli, and H. H. Weitering, Phys. Rev. B **59**, 15 779 (1999).

[27] D. A. Lavis and G. M. Bell, *Statistical Mechanics of Lattice Systems* (Springer, Berlin, 1999), Vol. 1.

[28] J. A. Stroscio, R. M. Feenstra, and A. P. Fein, Phys. Rev. Lett. **57**, 2579 (1986).

[29] J. A. Kubby, Y. R. Wang, and W. J. Greene, Phys. Rev. Lett. **65**, 2165 (1990).

[30] S. Eggert, A. E. Mattsson, and J. M. Kinaret, Phys. Rev. B **56**, R15537 (1997).

[31] T. Yokoyama and K. Takayanagi, Phys. Rev. B **59**, 12 232 (1999).