

## Electronic structure of Bi lines on clean and H-passivated Si(100)

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2010 J. Phys.: Condens. Matter 22 175006

(<http://iopscience.iop.org/0953-8984/22/17/175006>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 30/05/2010 at 07:53

Please note that [terms and conditions apply](#).

# Electronic structure of Bi lines on clean and H-passivated Si(100)

Jakub Javorský<sup>1,2</sup>, James Hugh Gervase Owen<sup>3</sup>, Martin Setvín<sup>1,2</sup>  
and Kazushi Miki<sup>1</sup>

<sup>1</sup> National Research Institute for Materials Science (NIMS), Tsukuba 305-0044, Japan

<sup>2</sup> Charles University, MFF KFPP, V Holešovických 2, 180 00 Praha 8, Czech Republic

<sup>3</sup> Département de Physique de la Matière Condensée, NCCR MaNEP, Université de Genève,  
24 Quai Ernest-Ansermet, 1211 Genève 4, Switzerland

E-mail: [jakub.javorsky@post.cz](mailto:jakub.javorsky@post.cz) and [miki.kazushi@nims.go.jp](mailto:miki.kazushi@nims.go.jp)

Received 6 November 2009, in final form 19 February 2010

Published 7 April 2010

Online at [stacks.iop.org/JPhysCM/22/175006](http://stacks.iop.org/JPhysCM/22/175006)

## Abstract

By means of scanning tunnelling microscopy and spectroscopy, we have investigated the electronic structure of Bi nanolines on clean and H-passivated Si(100) surfaces. Maps of the local density of states (LDOS) images of the Bi nanolines are presented for the first time. The spectra obtained for nanolines on a clean Si surface and the LDOS images agree with *ab initio* predicted spectra for the Haiku structure. For nanolines on a H-passivated surface, the spectra obtained suggest that the Bi nanoline may locally pin the surface Fermi level, and the LDOS images taken at low bias show a distribution of states different to what was expected at the Bi nanolines. The results are discussed with respect to use of the nanolines as atomic wire interconnections.

(Some figures in this article are in colour only in the electronic version)

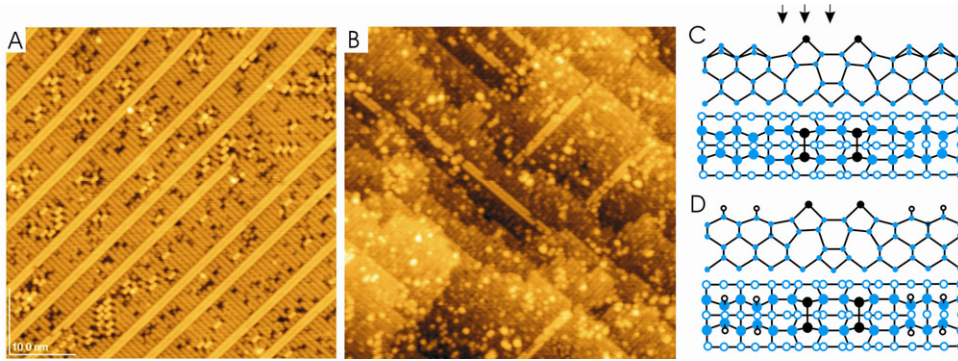
## 1. Introduction

In the last decade, considerable scientific attention has been focused on structures with two or all three spatial dimensions on the scale of single nanometres. While the assembly of various such structures has been investigated [1], it is mostly impractical due to the extreme time consumption of such processes. On semiconductors, nano-scale structures can be grown in mass numbers using surface irregularities such as step edges, anisotropic strain fields or growth kinetics. (Nanodots and nanowires created this way are now one of the most studied systems.)

Bismuth lines on the Si(100) surface have attracted a lot of attention. Unlike most other systems, Bi lines have a constant width of 15 Å, are perfectly straight, with practically no kinks or defects, can grow more than 1 μm long and their growth is not inhibited by step edges [2–4]. Examples are shown in figures 1(a) and (b). The structure of the nanoline is explained by the generally accepted Haiku model, shown in figure 1(c). In this model, the basic unit cell comprises two Bi dimers, underneath which the Si surface is reconstructed into 5- and 7-membered rings [3], hence the name ‘Haiku’. This structure is energetically more favourable by more than 0.37 eV/Bi

dimer than other proposed structures and is the only model which agrees with all the scanning tunnelling microscope (STM) observations, particularly the electronic contrast at low voltages [5]. The reconstruction of the underlying Si atoms in this model also explains why there are practically no kinks on the nanolines and why they do not grow together or sideways [3].

Two different electronic contrast effects are seen on the Bi nanoline in STM images on the clean surface. First, at biases within circa ±1 eV, the Bi nanolines appear darker than the surrounding Si surface but brighter at higher biases. Density functional theory (DFT) calculations of different Bi/Si structures indicate that at low biases, the density of states on the Bi dimers is very low compared to the surrounding Si surface, hence causing the change of contrast [5, 6]. Secondly, the Si dimers adjacent to a Bi nanoline appear enhanced (brighter) in STM images. The enhancement effect has been explained by DFT calculations as a result of strain of the atoms immediately surrounding the Haiku structure [5]. Passivation of the Si surface with hydrogen is reported to have no effect on the Bi nanoline [7], although in large doses, atomic H can remove the Bi dimers [8]. A recent *ab initio* calculation suggested that Bi nanolines on the H-terminated Si surface should be



**Figure 1.** Bi nanolines on (A) clean and (B) H-passivated Si(100).  $I_t = 0, 1$  nA;  $U_s = -1, 8$  V. Model of Haiku structure on (C) clean and (D) H-passivated Si(100) surface. Arrows mark positions where STS spectra were measured. Blue circles refer to Si, larger black circles refer to Bi, and open circles to H.

more suitable for application as atomic wires, since there is no current leakage from the nanoline to the substrate at low biases [9]. On both clean and H-terminated Si surfaces, Bi nanolines are reported to be semiconducting [10, 11]. The electronic structure of the Bi nanolines has been studied by Miwa, McLeod and Belosludov [9–11] by *ab initio* calculations, but no experimental paper has been published on this topic. In this paper, we present the first scanning tunnelling spectra (STS) and local density-of-states (LDOS) images of Bi nanolines on clean and H-terminated Si surfaces. The results are discussed with respect to the published *ab initio* calculations. We will show that for the clean Si surface, the predicted tunnelling spectra agree with measured spectra, but on the H-terminated surface the spectrum is different. Furthermore, our data explain the bias-dependent contrast of the Bi nanolines.

## 2. Experimental details

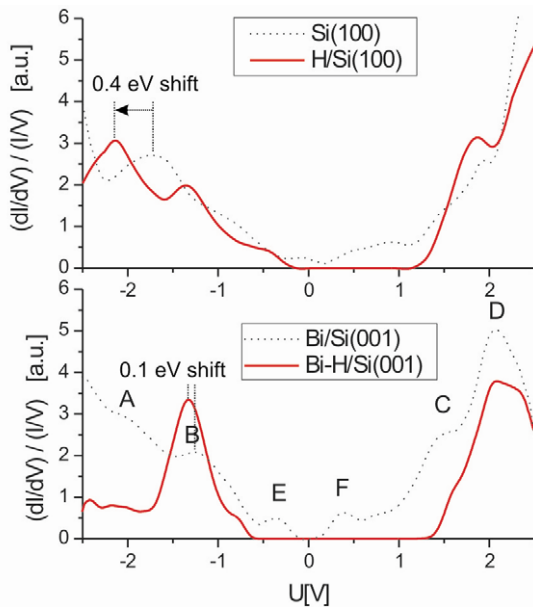
The Si(100)- $2 \times 1$  reconstruction was prepared *in vacuo* by flashing a boron-doped Si(100) sample with resistivity 0.01–0.1  $\Omega$  cm several times to 1200 °C in a base pressure better than  $3 \times 10^{-8}$  Pa. The condition of the surface was checked before deposition. Bi was evaporated from an effusion cell typically at 470 °C for 15 min, while the surface was kept at a little lower than 600 °C. After evaporation, the surface was kept at elevated temperature for another 15 min before cooling down to room temperature (RT). Passivation of the surface by atomic hydrogen was achieved by exposing the surface to 1000 l of hydrogen of 99% purity, dissociated to single H atoms by a hot filament. Measurements were conducted using a JEOL 4500 XT UHV STM. An electrochemically etched tungsten tip was cleaned *in situ* by electron bombardment and treated on a Pt crystal before each measurement to ensure the metallicity of the tip. Reproducibility was verified using different tips. The STS spectra and LDOS mapping were obtained by lock-in detection  $(dI/dV)/(I/V)$ . STS spectra were measured with the feedback loop open, the tip–sample distance was determined by setting  $V_s = -2.0$  V and  $I_t = 0.1$  nA before opening the loop. Each presented spectrum is an average of 10–20 spectra obtained at different equivalent

positions on the sample, in an area without any observable surface defects. The Bi nanoline was scanned at various voltages before choosing a site for the STS measurement to make sure that there was no contamination on the nanoline or in its proximity. The position of peaks in the spectra did not vary between individual experiments, though their width and/or height did vary slightly. The condition of the tip was checked during experiments by taking reference spectra of the clean Si substrate. The presented LDOS images were obtained using slightly different set-point currents to achieve the best image resolution and tip stability. The modulation frequency was 961 Hz and the amplitude was 30 mV. Images were obtained in constant current mode because of the height difference between the Si substrate and Bi nanolines. A small loop gain was selected so that the modulation would not affect the feedback loop.

## 3. Results and discussion

On the clean Si surface, the STS spectrum shows the commonly observed silicon peaks at  $-1.7$  eV,  $-0.85$  eV (originating from the dangling bond  $\pi$  states),  $+0.45$  eV (originating from the anti-bonding  $\pi^*$  states),  $1.5$  and  $1.9$  eV (mixed states related mainly to backbond orbitals with contributions from  $\pi^*$  and  $\sigma$  orbitals [12]). After passivation, the peak at  $+0.45$  eV and other smaller states near the Fermi level disappeared, since the dangling bonds became saturated with H atoms. The  $+1.5$  and  $+1.9$  eV states do not change, but the  $-0.85$  and  $-1.7$  eV states are moved to  $-1.3$  and  $-2.1$  eV. This peak shift can be explained by tip-induced band bending as follows: on the p-type clean Si(001)- $2 \times 1$ , tip-induced band bending is limited by the valence band maximum (VBM) and the  $\pi^*$  state to circa  $(-0.15; +0.18)$  eV from the Fermi level [13]. But when we passivate the Si dimers with hydrogen, the  $\pi^*$  state disappears and the shift of the *filled* states due to tip-induced band bending is practically limited only by the width of the band gap. The shift of the *empty* states will still be limited by the VBM. This corresponds well with the observed shift of the filled states by  $\sim 0.4$  eV and almost zero shift of the empty states.

The Bi spectrum is dominated by large peaks at  $-1.9$  eV (labelled A)  $-1.25$  eV (B),  $+1.45$  eV (C) and  $+2.0$  eV (D),

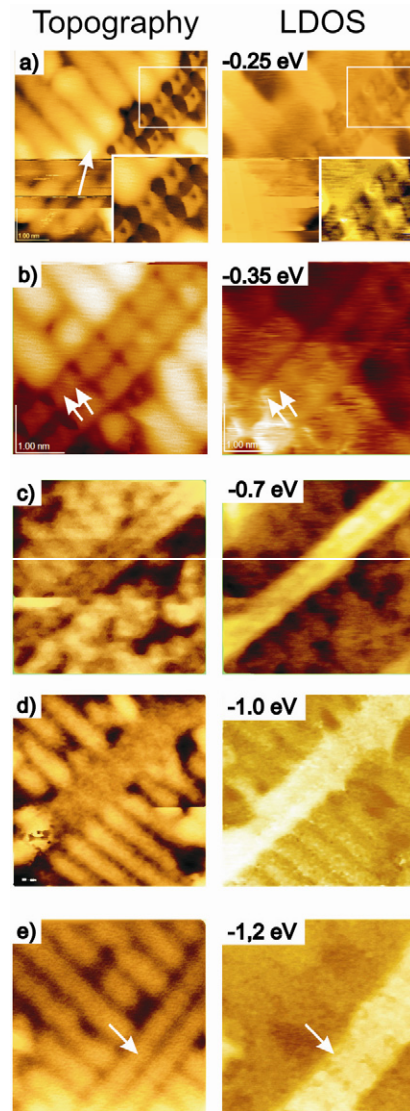


**Figure 2.** STS spectra taken on clean and H-terminated Si(100) surface. The arrow marks the tip-induced band bending. Letters A–F mark the peaks discussed in the text.

and two smaller peaks near the Fermi level at  $-0.38$  eV (E) and  $+0.37$  eV (F). The positions of the peaks correspond well with the predicted spectra [9] for the Haiku structure. The measured spectra support the reported explanation of change of contrast: the Bi nanoline appears darker than the silicon substrate in topographic images at low bias, because the large bismuth peaks are located further from the Fermi level than Si peaks.

The spectrum obtained on the Bi lines on the H-passivated Si(100) surface is quantitatively different. The band gap broadens to ca 2 eV. The Bi line spectrum is dominated by a peak at  $-1.35$  eV and the peaks within  $\pm 0.5$  eV (E, F) of the Fermi level are washed out. This is in agreement with theoretical predictions by Miwa *et al* [10]. The fact that the filled state Bi peak shifts only by 0.1 eV after passivation (while the peaks on the Si substrate shift by 0.4 eV, see figure 2) indicates that the Bi nanoline locally pins the Fermi level and prevents the tip-induced band bending. The A and C peaks that were present on the clean surface at  $-1.9$  and  $+1.45$  eV disappear completely. The spectrum predicted in [10] indicates peaks around  $-1.3$  and  $-1.8$  eV (please note that we set zero energy as the Fermi level, while in [10] the zero energy corresponds to the highest occupied peak which is  $\sim -0.7$  eV in our notation). Comparing our experiments and the prediction, we can attribute the  $-1.3$  eV peak to the Bi nanoline and the  $-1.8$  eV peak to the H-passivated substrate. The difference between the measured ( $-2.1$  eV) and predicted ( $-1.8$  eV) position of the substrate-related peak agrees well with the observed tip-induced band bending of 0.4 eV.

Figure 3 shows a series of topographic and LDOS images on non-passivated surface. The Si dimer rows are resolved as bright stripes in the topographical image running from the top left corner to the bottom right. The Bi nanolines run from top right to bottom left. One line consists of two bright stripes. The

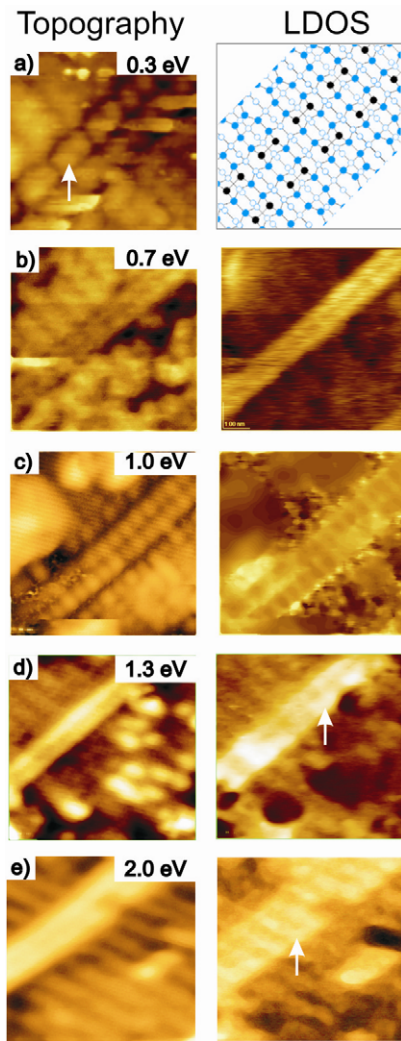


**Figure 3.** Filled state images of Bi nanolines on clean Si(100). Arrows mark features discussed in the text.

voltage dependence of the images supports our explanation of the charge contrast. Very little density of bismuth states is present below  $-0.7$  eV that could contribute to the topography image, so the Bi nanoline appears darker than the substrate even though it is morphologically higher.

Comparing our measurements with the *ab initio* calculations performed by McLeod, Miwa and Owen [5, 10, 11], the small bismuth peak (E) at  $-0.38$  eV can be attributed to the very localized pairs of protrusions above the Bi dimers (figure 2 and arrow in figure 3(b)). The rather broad peak (B) at  $-1.25$  eV is composed from two components, the energetically lower-lying  $\pi^*$ -like states above Bi atoms and the higher-lying  $\sigma$ -like states forming the Bi–Bi bond (figure 2 and arrows in figure 3(e)). Note that the Bi states begin to overlap themselves and onto the neighbouring Si dimers above  $-1.0$  eV.

In figure 3(a) (see arrows), the brightness enhancement of Si dimers adjacent to the Bi nanoline is visible in the topographical image, but in the LDOS image the Si dimers adjacent to the Bi nanoline are darker than the other Si dimers.

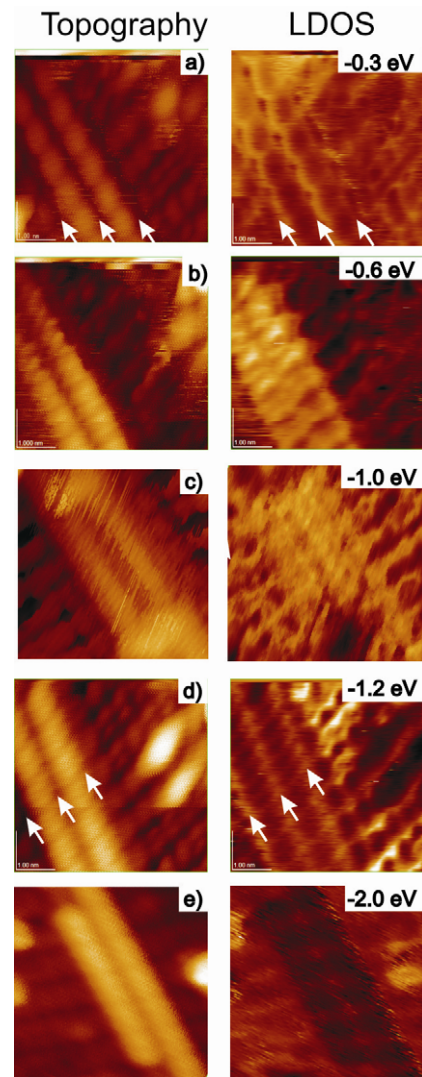


**Figure 4.** Empty state images of Bi nanolines on clean Si(100). Arrows mark features discussed in the text.

This suggests that the charge density on the Si dimers adjacent to the Bi nanoline moves towards lower energies and that the enhancement effect occurs at energies below  $-0.25$  eV.

Figure 4 shows topography and LDOS images of Bi nanolines in empty states. Only weak states are located on Bi nanolines up to  $+0.9$  eV, appearing as highly localized oval-shaped protrusions above Bi atoms (see arrow in figure 4(a)). At  $+1.3$  eV another Bi state appears with maximum contrast with respect to Si (figure 4(d)). It stretches along the Bi nanoline from one pair of Bi dimers to another and overlaps the neighbouring Si dimers. The state at ca  $+2.0$  eV also overlaps Si dimers but it is shaped as a bright protrusion joining the Bi dimers of the two stripes forming the nanoline. Due to problems with tip stability, it was not possible to obtain any LDOS images at very low positive bias (0.3 eV).

Figure 5 shows topography and LDOS images of Bi nanolines on the H-terminated Si(100) surface. Hydrogen atoms saturating the Si dangling bonds are resolved as round protrusions throughout the range of observed bias voltage. At  $-0.3$  eV, the Bi nanoline appears as two stripes of protrusions located above the Bi dimers. However, in the corresponding



**Figure 5.** Filled state images of Bi nanolines on H-terminated Si(100). Arrows mark features discussed in the text.

DOS image, there are dark areas instead of the protrusions. Three bright lines can be seen, two at the sides of the Bi nanoline and one in the middle (see arrows in figure 5(a)). By comparison of the image with a model of the Haiku structure, we can see that these states are located above the four Si atoms that connect the Bi dimer to the Si dimer row and the four Si atoms between two Bi dimers (see the model in the inset of figure 3(a)). Interestingly, the Haiku structure does not predict any bond in the first layer of Si atoms that would run parallel to the Bi nanoline, as do these states. The dark areas above Bi dimers in the DOS image indicate that a lower-lying state should exist on the Bi dimers to explain the bright blobs in topographic images.

At  $-0.6$  eV, Bi states appear as double oval protrusions localized above the Bi atoms. The shape of the state and its energy correspond to the  $\pi$ -like state described by the *ab initio* calculation by Miwa *et al* [10]. Around  $-1.0$  V, more states appear on the H-terminated silicon surface and the contrast of the substrate in DOS images with respect to the Bi nanoline decreases.

At  $-1.2$  eV the LDOS image looks very similar to the image at  $-0.3$  eV, but a closer look reveals that protrusions (marked by arrows) are located between the two Si atoms connecting a Bi atom to Si dimer row and between the two Si atoms in the middle of the nanoline. As the energy of these states is close to the Si dimer bond energy on the clean Si(100) surface, we suppose these states are bonding states of the two Si atoms. No Bi states appear at  $-1.2$  eV (figure 5(d)), in agreement with the observed STS spectrum.

At higher energies, the contrast in LDOS image between the Bi nanoline and H-terminated substrate reverses and the Bi nanoline appears dark. In the topographic images, however, where the contrast is produced as an integral over all states up to the selected voltage and where the topographical information plays more important role, the Bi nanolines still appear brighter than the H-terminated silicon substrate.

We were not able to obtain any reliable data in empty states on the H-terminated surface, as the tip was not stable enough to take DOS images at these voltages.

#### 4. Conclusions

We measured STS spectra and LDOS (density-of-states) images of Bi nanolines on clean and H-terminated Si(100) surfaces. On the clean Si(100) surface, the measured STS spectra match well with spectra predicted with *ab initio* calculations. However, on the H-terminated surface the predicted spectrum shows one more major peak than was experimentally observed and states unexplained by the calculations appear in the DOS images. Enhancement of the brightness of the Si dimers adjacent to Bi nanolines was observed and energies at which the enhancement takes effect were narrowed to within  $\pm 0.2$  eV from the Fermi level. Our results show that the Bi nanoline is semiconducting. Strong, overlapping bismuth states appear in the regions  $+0.9$ – $2.0$  eV and  $-0.7$  to  $-2.0$  eV on the clean surface. Furthermore, these states overlap the neighbouring Si dimers, which could lead to possible current leakage should the nanoline be used as a conducting wire [9]. On the H-passivated surface the

bismuth states remain localized to the nanoline and no current leakage to the substrate should occur. Therefore, the bismuth nanoline on the H-passivated Si(100) could be used as an atom-wire interconnection for molecular devices or as a template for deposition of other materials that will have conducting properties.

#### Acknowledgments

This research was partially supported by the Ministry of Education, Science, Sports and Culture (MEXT), Grant-in-Aid for Scientific Research (A), 19206003 and A3 Foresight Program from the Japanese Society for the Promotion of Science. JJ would like to thank NIMS for his stay with the NIMS Internship Program. We acknowledge Mr Liu Hongjun for his technical assistance.

#### References

- [1] Eigler D M and Schweizer E K 1990 *Nature* **344** 524–6
- [2] Miki K, Owen J H G, Bowler D R, Briggs G A D and Sakamoto K 1999 *Surf. Sci.* **421** 397
- [3] Owen J H G, Miki K, Koh H, Yeom H W and Bowler D R 2002 *Phys. Rev. Lett.* **88** 226104
- [4] Owen J H G, Miki K and Bowler D R 2006 *J. Mater. Sci.* **41** 4568
- [5] Owen J H G, Miki K and Bowler D R 2003 *Surf. Sci.* **527** L177–83
- [6] Miwa R H, Schmidt T M and Srivastava G P 2002 *Surf. Sci.* **507–510** 368–73
- [7] Owen J H G, Bowler D R and Miki K 2002 *Surf. Sci.* **499** L124–8
- [8] Wang Q H and Hersam M C 2008 *J. Am. Chem. Soc.* **130** 12896
- [9] Belosludov R V, Farajian A A, Mizuseki H, Miki K and Kawazoe Y 2007 *Phys. Rev. B* **75** 113411
- [10] Miwa R H, MacLeod J M, McLean A B and Srivastava G P 2005 *Nanotechnology* **16** 2427
- [11] MacLeod J M, Miwa R H, Srivastava G P and McLean A B 2005 *Surf. Sci.* **576** 116
- [12] Dubois M *et al* 2005 *Phys. Rev. B* **71** 165322
- [13] McEllistrem M 1993 *Phys. Rev. Lett.* **70** 2471