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Abstract. The Na–Si(111) 3 × 1 and Na–Si(111) interfaces with various coverages of Na have been investigated using low-energy electron diffraction Auger electron spectroscopy and photoemission spectroscopy (PES) with a synchrotron radiation source. In decomposing the PES peak from the Si 2p core level into the surface and bulk components, the relative shifts and intensities of the surface components as well as the band bending for the 3 × 1 interface are consistent with the structure model proposed by Mönch. The evolution of the band bending from about 1 monolayer to thick Na coverage corresponds to the theory of the metal-induced gap states. The final Schottky barrier height is determined to be 0.38 ± 0.05 eV and does not depend on whether a thicker Na layer is deposited on an ordered Na–Si(111) 3 × 1 surface or a disordered thin Na layer on Si(111).

1. Introduction

Because of the simple electronic structure of alkali metals, which do not form silicides at the metal–Si interface, the use of alkali-metal atoms for studying the interaction between a metal and a semiconductor, the properties and the formation of the Schottky junction is attractive. To understand the electronic structure of alkali-metal–silicon interfaces, well ordered alkali overlayers on a silicon surface are preferentially used. On the cleaved Si(111) 2 × 1 surface, Cs adsorption has been studied at room temperature with a $\sqrt{3} \times \sqrt{3}$ reconstruction structure [1]. Uhrberg and Hansson [2] derived the surface state band structure from [1]. Daimon and Ino [3] firstly observed by reflection high-energy electron diffraction the 3 × 1 reconstruction induced by alkali metals adsorbed on the Si(111) 7 × 7 surface at the annealing temperature. Hashizume *et al* [4] also reported the result of K 3 × 1 on the Si(111) surface. Tikhov *et al* [5] first gave the result of a sodium-induced 7 × 7-to-3 × 1 transition on the Si(111) 7 × 7 surface by low-energy electron diffraction (LEED) and electron energy loss spectroscopy. Jeon *et al* [6] studied the same structure using scanning tunnelling microscopy (STM) and suggested that two Na atoms are contained in each 3 × 1 unit cell. They [7] proposed that the reconstruction of 3 × 1 on Si(111) is due to the arrangement of sodium atoms adsorbed, while Fan and Ignatiev [8] argued that the 3 × 1 reconstruction is due to the missing row in top-layer atoms of Si(111) and alkali atoms are adsorbed in a disordered manner on the Si surface. However, this problem is still open.

The key physical quantity characterizing the interface of metals and semiconductors is the Schottky barrier height (SBH), the formation of which is an old problem but still not completely resolved. Successfully using the concept of the 'neutrality level' of the theory of metal-induced gap states (MIGS), Tersoff [9] developed a quantitative theory which agrees well with the experimental results on the SBH for gold contacts with various semiconductors. Mönchl [10] suggested the MIGS-plus-defects model which can account for a large number of the experimental data on the SBH for various metal contacts with silicon. It is a very interesting problem for both practical and basic research. In this paper, we report our investigation on the Na 3×1–Si(111) 7×7 interface by Si 2p photoemission and discuss the intensities and shifts of the surface components in connection with the possible interface structure as well as on the evolution of the SBH in comparison with the MIGS theory.

2. Experimental details

The experiment was performed in a UHV chamber with an integrated hemispherical electron analyser (VSW Company) at the National Synchrotron Radiation Laboratory, Hefei, People's Republic of China. The radiation of the beam line U20A was monochromated with a SGM monochromator. The base pressure in the chamber was 3×10^{-8} Pa. An n-type (phosphorus-doped (about 5×10^{18} cm^{-3})) Si(111) sample was degassed at 800 °C overnight and repeatedly annealed to 1000 °C to obtain a clean surface which was checked by Auger electron spectroscopy. Neither carbon nor oxygen contamination was detected. After annealing, the sharp 7×7 LEED pattern of a clean Si(111) surface was obtained. To avoid the bombardment effect on the SBH, Ar$^+$ sputtering was not used. Sodium was evaporated from a commercial alkali metal dispenser (SAES Getters, Italy). Two different substrate temperatures during Na deposition were used to achieve a conversion of 7×7 to 3×1. In one method the substrate was at room temperature during Na deposition and then was annealed to the appropriate temperature to get the 3×1 LEED pattern in the same way as Tikhov *et al* [5]. The other method used is due to Jeon *et al* [6] in which the substrate was annealed to 350 °C during Na deposition.

The changes in the band bending of Na/Si(111) at various Na coverages were measured using the Si 2p core-level photoelectron spectra. The Si 2p integrated photoelectron spectra were taken for two photon energies 109 and 135 eV.

3. Results and discussion

The LEED pattern of the Na-induced 3×1 reconstruction on Si(111) is shown in figure 1. We obtained Si(111) 3×1 in both the methods mentioned above. The annealing conditions are crucial for the substrate on which Na is deposited at room temperature. It is easy to observe the process of 3×1 formation by annealing the substrate to 350 °C during Na deposition. The reconstruction on the surface has three kinds of domain with symmetries rotated relative to each other by 120 °C. Annealing is necessary for the surface atoms to overcome the dimer potential and to arrange in an orderly manner to a 3×1 structure.

By tuning the photon energy, photoelectrons can provide different escape depths for bulk-sensitive or surface-sensitive measurements. In our case, the Si 2p core-level spectra were measured with photon energies of 109 eV (escape depth, about 13 Å; bulk sensitive) and 135 eV (escape depth, about 4 Å; surface sensitive). The spectra of photon energy 135 eV contain more information from the surface layer. The spectra of photon energy
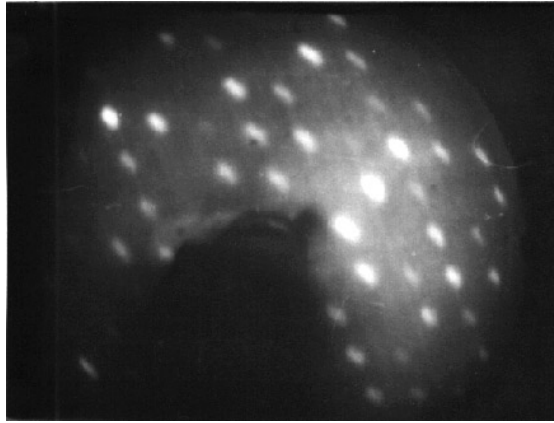
Figure 1. The 3 × 1 LEED pattern of Na/Si(111). $E_p = 109$ eV.

109 eV are bulk sensitive and are used to measure the changes in band bending. To avoid any effect of the beam shifts, we took each Na-doped Si 2p spectrum immediately after the Si 2p spectrum of clean Si(111) at the photon energy 109 eV.

In figure 2(a) the Si 2p spectrum of the clean Si(111) 7×7 is shown to be in agreement with those obtained by others, e.g. Karlsson *et al* [11]. When the 3×1 reconstruction was obtained by annealing the substrate to 350 °C during Na deposition (denoted hereafter as AT), the Si 2p spectrum shown in figure 2(b) was obtained. The Si 2p spectrum after Na deposition at room temperature without annealing (denoted hereafter as RT) is shown in figure 2(c). The spectra are taken with the photon energy 135 eV and fitted with one bulk component and two surface components using a non-linear least-squares method. Each component has spin–orbit splitting. The numerical parameters are listed in table 1. The shifts of S_2 (or S_2') relative to the bulk peak B are 0.7, 0.5 or 0.38 eV towards a lower binding energy for clean Si, AT and RT, respectively. In figure 2(d), the spectrum is taken with a photon energy 109 eV. The Gaussian widths are around 350 meV.

For clean Si(111) 7×7, Karlsson *et al* [11] labelled the S_2 peak as the rest atoms while Chiang and co-workers [12] assigned it to the adatoms. Paggel *et al* [13] demonstrated, using high-resolution core-level spectroscopy, the presence of four surface-derived components in the Si 2p line, which correspond essentially to the assignment made by Karlsson *et al*. Their criterion is that the different types of Si atom give different core-level binding energy peaks and the peak areas (evaluated for different photon energies) are associated with the number of atoms of the corresponding type.

Concerning the structure of the Na/Si(111) 3×1 surface, several models have been proposed. In the model of Jeon *et al* [6], the top-layer atoms are all Na, with a coverage of 2/3, but other groups have reported much lower measured values of Na coverage [8, 14]. In the missing-row model proposed by Fan and Ignatiev [8], some Si atoms of the second and third layers have broken bonds. It seems unlikely that such a structure can have the minimum energy. Mönch [10] proposed a structure model for M/Si(111) 3×1 shown in figure 3, which seems to us more reasonable. In the following, we discuss our results in connection with this possible structure.

We note that the S_2' peak grows during Na deposition before saturation. This phenomenon indicates that the S_2' peak is due to Si atoms adjacent to Na atoms. The shifts of S_2' towards lower binding energy show that the Si atoms are electron rich. On the
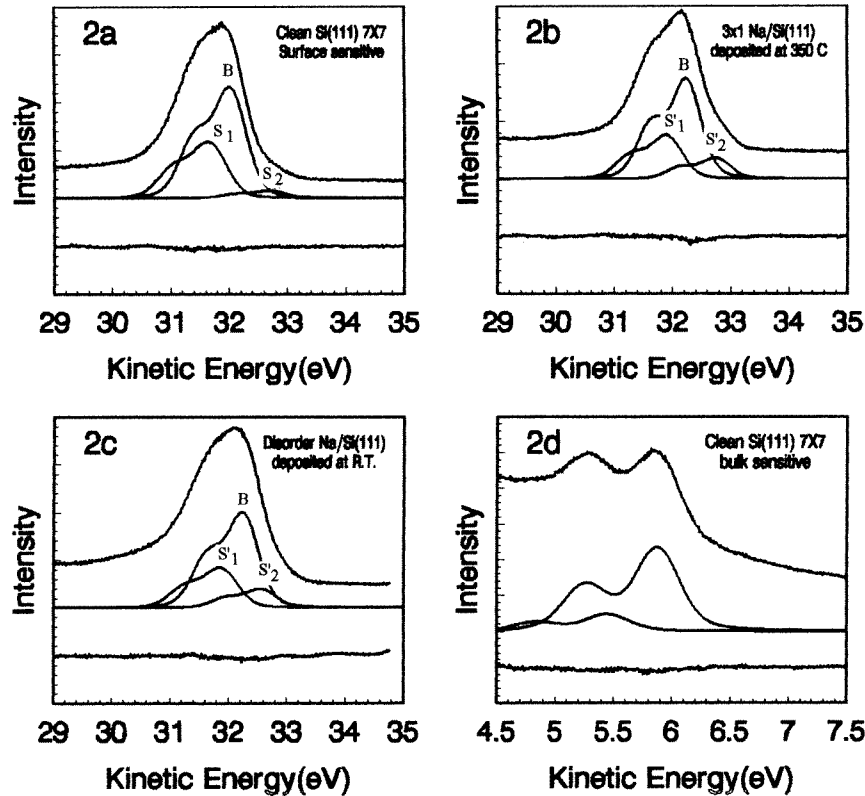
Figure 2. The Si 2p core-level spectra taken at 135 eV for (a) clean Si(111) 7 × 7, (b) for Na deposition at the annealing temperature and (c) for Na deposition at room temperature. (d) One of the spectra taken with the photon energy 109 eV, which shows that the Gaussian widths are about 350 meV. All spectra are fitted with a non-linear least-squares method and the bottom curve in each picture is the difference between the experimental curve and fitted components.

basis of the Mönch [10] model we ascribe the S'_2 component of those Si atoms which are situated just below the Na atoms. The peak S'_2 shifts to lower binding energy relative to the bulk peak by the covalent bonding of Na–Si with some charge transfers to Si. In table 2, our results are compared with those of Paggel *et al* [13]. It can be seen that the ratio of the S'_2 peak area to the S'_1 peak area is about 0.5 in our results and about 1 in the data of Paggel *et al* . Considering the escape depths (different photon energies), this difference is reasonable since the Na atom above the S'_2 atom attenuates substantially the intensity of the S'_2 photoelectron in our case (escape depth, about 4 Å) but only a little in the case of Paggel *et al* (escape depth about 9 Å, and measured in the normal direction).

According to Mönch's model (figure 3), there are two top-layer Si atoms and one S'_2 atom in one unit cell of the surface. Thus the nearly equal peak areas of S'_1 and S'_2 in the results of Paggel *et al* is puzzling. This, however, can be resolved if one notices that the Si dimers in the top layer are asymmetric (asymmetric dimers can give lower total energy than symmetric dimers). It can be argued that some electronic charge will transfer from the Si atom relaxing inwards to the Si atom relaxing outwards. We ascribe the S'_1 component of the Si 2p core level to the atoms to relaxing inwards, which are deficient in electrons and

Table 1. Numerical parameters for the fit of the Si 2p.

	Clean at $h\nu = 135$ eV	3×1 at $h\nu = 135$ eV	At RT at $h\nu = 135$ eV
Spin–orbit split	0.614	0.614	0.614
Branching ratio	0.55	0.55	0.55
Bulk			
KE	32.021	32.240	32.253
Gaussian width	0.55	0.50	0.54
Lorentzian width	0.15	0.15	0.15
Intensity	0.622	0.597	0.619
S_1, S_1'			
Core shift	−0.356	−0.342	−0.354
Gaussian width	0.59	0.54	0.58
Lorentzian width	0.15	0.15	0.15
Intensity	0.334	0.274	0.278
S_2, S_2'			
Core shift	0.686	0.502	0.380
Gaussian width	0.55	0.50	0.54
Lorentzian width	0.15	0.15	0.15
Intensity	0.044	0.129	0.104

Table 2. The result of the ratio of the S_2' peak area to the S_1' peak area compared with the data of Paggel *et al.*

Reference	S_2'-to-S_1'-peak-area ratio	Photon energy (eV)	Escape depth (Å)	Direction of photons
Paggel *et al* [13]	$\simeq 1$	122	$\simeq 9$	Normal
This work	$\simeq 0.47$	135	$\simeq 4$	Integrated

give an intensity of S_1' nearly equal to that of S_2'. (Although the Si atoms relaxing outwards should also cause another surface component, this component may not be resolved from the bulk component due to the compensating effects of the charge transfer from S_1' atoms and of the absence of upper atoms.)

Figure 4 shows the variations in band bending, which relative to the clean surface for both AT and RT are measured with reference to the Fermi level by the shift of the Si 2p peak at the photon energy 109 eV relative to the case of the clean Si 7×7 surface, as a function of the peak area ratio of Na 2p to Si 2p (photon enegy, 135 eV). The reason for using this abscissa is to avoid a large error in the deposition quantity. The calibrated coverage of Na using a similar formula to that of Karlsson *et al* [11] with the photoionization cross section at the photon energy of 109 eV [15] is also shown in figure 4. According to STM and photoemission results [14], each 3×1 unit cell contains one Na atom (the coverage is 1/3). One can see from figure 4 that the maximum value of the band bending for AT occurs when the area ratio of Na 2p to Si 2p is about 0.02 and amounts to $E_c^s - E_f \simeq 0.66$ eV (i.e. $E_f - E_v^s \simeq 0.48$ eV). It should not equal the value for the cleaved Si(111) 2×1 surface due to the surface reconstruction induced by Na. However, this value is close to the Fermi-level pinning position of the cleaved Si(111) 2×1 surface [16]. This can be explained as follows. For n-type semiconductors, the Fermi level at the surface is pinned by the acceptor-like surface states which the Na atoms cannot provide. Thus the pinning
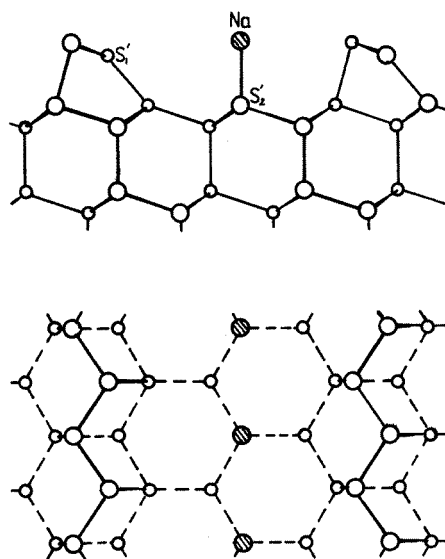
Figure 3. The scheme of the Na/Si(111) 3×1 model suggested by Mönch [10]. The S'_1 and S'_2 silicon atoms correspond to the S'_1 and S'_2 peaks, respectively.

surface states must be derived from the dangling bonds of the Si atoms in the first layer. The arrangement of these atoms, as shown in figure 3, resembles very much that of Si(111) 2×1 with a zigzag chain. Hence the pinning position of our results should be close to that of Si(111) 2×1, and this agreement supports indirectly the Mönch model for Na/Si(111) 3×1. In the RT case, one can find the maximum band bending of the same amount when the ratio of Na 2p to Si 2p is about 0.04, which corresponds roughly to the coverage 1/3 monolayer (ML).

Beyond the coverage 1/3 ML for the RT case, the barrier height drops sharply, but tends to a lower constant value when the coverage approaches 1 (Na 2p to Si 2p ratio of
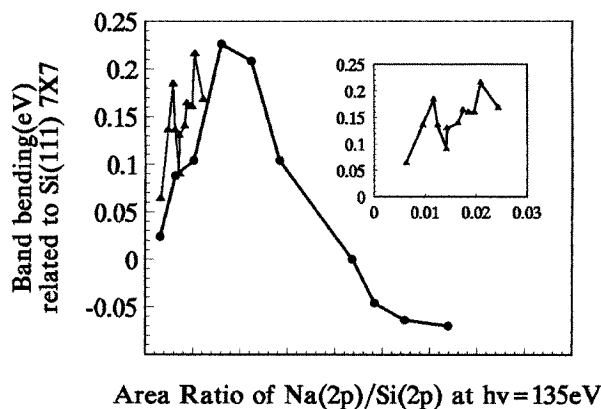

Figure 4. The band bending ($h\nu = 109$ eV) against the area ratio of Na 2p to Si 2p at $h\nu = 135$ eV for RT ($\bullet$) and AT ($\blacktriangle$). The insets show the enlarged AT results in detail.
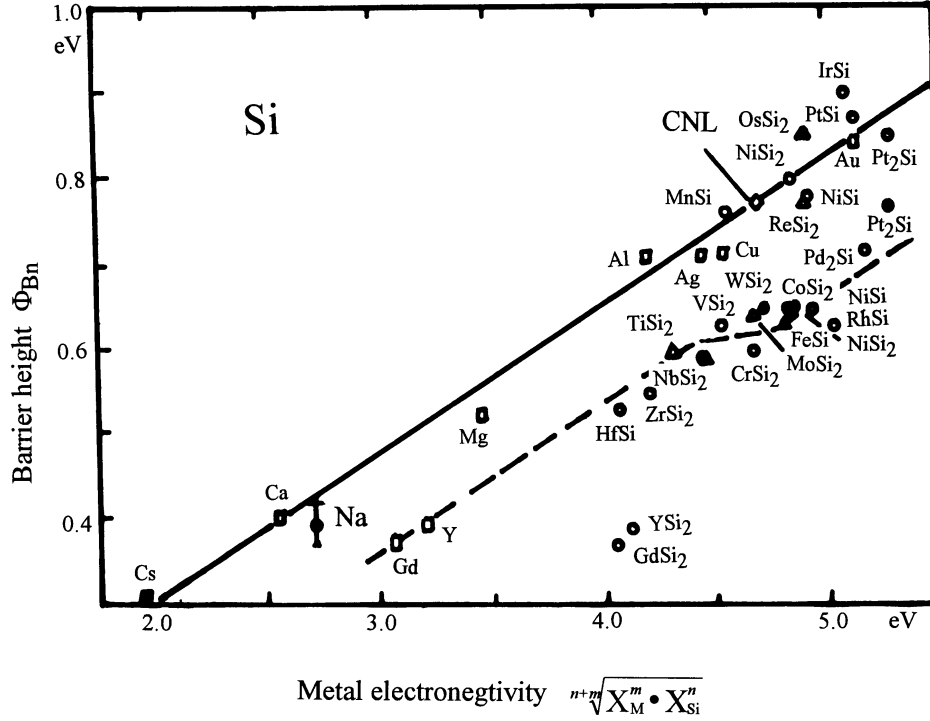
Figure 5. Barrier heights of metal–Si interfaces versus metal and silicide electronegativities (adapted from [10]): ● , our result.

about 0.135). This may be interpreted by the gradual formation of the Na metal layer. For comparison with the MIGS theory, thick Na (about 2.7 ML) in addition is deposited at room temperature on Na/Si(111) 3 × 1. The band bending changes to about −0.03 eV (relative to 0.47 eV for the clean n-type Si(111) 7 × 7 [16]). Since the carrier concentration of our sample is rather high, the Fermi level coincides roughly with the bulk conducting band minimum just as in the case in [11]. The difference is about 0.04 eV. This means that the SBH is about 0.40 ± 0.05 eV. In the RT case, the bending under thick Na coverage moves to −0.07 eV (relative to Si(111) 7 × 7, also). Then the SBH is about 0.36 ± 0.05 eV. The final values of the band bending are nearly the same. This reveals that the band bending does not depend on the interface structure very much. Taking the average of the AT and RT cases the SBH $\Phi_{Bn} \simeq 0.38 \pm 0.05$ eV for Na/Si(111) (n type). Here we label our result on the diagram of barrier heights versus metal electronegativities, shown in figure 5, for silicon [10]. In Tersoff's calculations, for Si the barrier height without a dipole layer in the interface is $\Phi_{Bn}^{(0)} = 0.76$ eV [9]:

$$\Phi_{Bn} = \Phi_{Bn}^{(0)} + S_x(X_m - X_{sub})$$

where $X_m - X_{sub}$ is the difference between the electronegativities of the metal and the semiconductor substrate in contact. The electronegativities are 2.70 and 4.70 for Na and Si, respectively. Thus,

$$S_x = \frac{\Phi_{Bn} - \Phi_{Bn}^{(0)}}{X_m - X_{sub}} = \frac{0.38 - 0.76}{2.70 - 4.70} = \frac{0.38}{2} = 0.19.$$

This value of S_x is close to the slop of Mönch's plot. Hence, the results of the SB formation at the Na–Si(111) interface are in good agreement with MIGS theory.

4. Conclusions

The 3×1 structure on Si(111) induced by Na adsorption is studied with Si 2p core-level photoemission. The shifts and the relative intensities of the surface components as well as the band bending at a coverage of 1/3 are in agreement with Mönch's structure model for M/Si(111) 3×1, in which the Na atoms are situated in the troughs of the Si(111) surface. The two surface components S'_1 and S'_2 are tentatively assigned to two kinds of Si atom in the structure model. The barrier height variation in the Si(111) surface due to sodium deposition shows that the SBH for thick Na is in agreement with MIGS theory and does not depend very much on the interface structure.

Acknowledgments

References

[1] Magnuson K O and Reihl 1989 *Phys. Rev.* B **39** 10 456
[2] Uhrberg R I G and Hansson G V 1991 *Crit. Rev. Solid State Matter Sci.* **17** 133
[3] Daimon H and Ino S 1985 *Surf. Sci.* **164** 320
[4] Hashizume T, Motai K, Hasegawa Y, Sumita I, Tanaka T, Amano S, Hyodo S and Sakurai T 1991 *J. Vac. Sci. Technol.* B **9** 745
[5] Tikhov M, Surnev L and Kiskinova M 1991 *Phys. Rev.* B **44** 3222
[6] Jeon D, Hashizume T, Wang X, Bai C, Motai K and Sakurai T 1992 *Japan. J. Appl. Phys.* **31** L501; 1993 *Appl. Surf. Sci.* **67** 257
[7] Jeon D, Hashizume T and Sakurai T 1992 *Phys. Rev. Lett.* **69** 1419
[8] Fan W C and Ignatiev A 1990 *Phys. Rev.* B **41** 3592; 1993 *Surf. Sci.* **296** 352
[9] Tersoff J 1984 *Phys. Rev. Lett.* **52** 465
[10] Mönch W 1993 *Semiconductor Surfaces and Interfaces* (Berlin: Springer)
[11] Karlsson C J, Landemark E and Johansson L S O 1990 *Phys. Rev.* B **41** 1521
[12] Miller T, Hsieh T C and Chiang T-C 1986 *Phys. Rev.* B **33** 6983
     Carlisle J A, Miller T and Chiang T C 1992 *Phys. Rev.* B **45** 3811
[13] Paggel J J, Theis W, Horn K, Jung Ch, Hellwig C and Petersen H 1995 to be published
[14] Paggel J J, Haak H, Theis W and Horn K 1993 *J. Vac. Sci. Technol.* B **11** 1439
[15] Yeh J J and Lindau I 1985 *At. Data Nucl. Data Tables* **32** 1
[16] Himpsel F J, Hollinger G and Pollak R A 1983 *Phys. Rev.* B **28** 7014