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Characteristics of potassium diffusion and adsorption on perfect and stepped GaAs(110) surfaces

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Abstract. We have used a self-consistent semi-empirical molecular orbital method to investigate whether the adsorption properties of K atoms and formation of the K adsorbate chains or clusters in the low-coverage regime can be influenced by the nature of the semiconductor surface: perfect or stepped. In the process, we are able to determine the microscopic structures of monatomic and diatomic K molecules on perfect and stepped GaAs(110) surfaces. Our results for K adsorption on the perfect GaAs(110) surface are consistent with recent scanning tunnelling microscopy (STM) observations for Na on GaAs(110), with the stable site for K being the bridge site encompassing one Ga and two As surface atoms. The equilibrium geometry for diatomic K has the second K atom occupying the next-nearest-neighbour bridge site, strongly supporting the formation of an open linear structure parallel to the surface atomic zigzag chains. The calculated K–K distance in this equilibrium configuration is 8.02 Å, similar to the Na–Na distance (8 Å) from the STM experiment. Our results for the stepped GaAs(110) surface suggest that a step is unlikely to assist clustering of K atoms, but, the formation of the linear adsorbate chain appears rather to be influenced by the orientation of the steps. However, the K adsorbates are bound more strongly at the steps than at the bridge sites on the perfect surface.

1. Introduction

Despite extensive work on metal–semiconductor interfaces [1–7], many of the interactions related to growth and nucleation are still not well defined. Some of these phenomena involve interactions at low metallic coverage, of relevance to the mechanism of Schottky barrier formation for instance. Moreover, different metallic atoms exhibit different adsorption characteristics, with some remaining apart [8, 9] while others show a great tendency towards clustering [2, 10]. Recent experimental observations via scanning tunnelling microscopy (STM) have also been inconclusive with regard to the determination of the preferred adsorption sites for these metals, with some metals, e.g. Au, Cs and Sm [1, 8, 9], exhibiting a definite preferred site, that is, at the surface Ga site at low coverage, while for other metals such as Fe, K and Al [2, 6, 10], the situation is not so clear. The adsorption mechanisms of these metals, whether similar or different, should depend strongly on the chemical interactions between the adsorbed metal atoms and the surface. If the metals are highly reactive, they may disrupt the surface to a considerable extent, but, if weakly interacting, the surface is relatively undisturbed with the metal atoms often clustering together [10] (growth by island formation, e.g. Al). Even present understanding of the mechanism for clustering is still not clear, although recently, Allan and Lannoo [11] have proposed that individual adatom–substrate bonds may exhibit a negative- U behaviour leading to adatom

pairing. However, they do not discount the possibility that formation of a covalent bond between pairs of adatoms can also lead to pairing [11].

Recently, adsorption of Na on the GaAs(110) surface was studied by field ion STM [12]. Prior to this investigation, the stable atomic position of adsorbed Na on GaAs(110) had not been established. In this study [12], Na adatoms are observed to reside on the bridge site encompassing one Ga and two As surface atoms to form linear chains along the $\langle 110 \rangle$ direction at low coverage. The Na–Na nearest-neighbour distance in this low-density chain structure is 8 Å along the $\langle 110 \rangle$ direction (see figure 1). In addition, no high-density two-dimensional ordered structures or low-density zigzag chains are observed, in contrast to the Cs/GaAs(110) system [8]. The formation of the ordered one-dimensional chain at low coverage suggests that Na atoms can move freely on the GaAs(110) surface at room temperature and that repulsive interactions along the $\langle 001 \rangle$ direction are significant at low coverage. However, the stable atomic position for K adsorbed on GaAs(110) is still not known experimentally although it is expected to behave like Na.

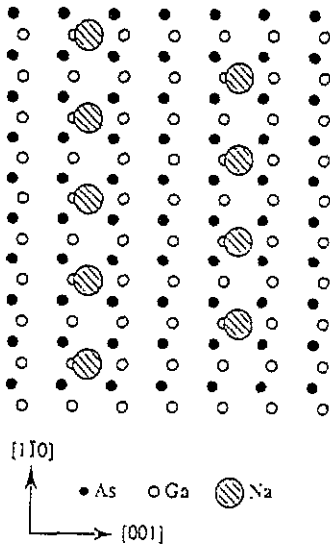


Figure 1. Schematic representation of linear (one-dimensional) chain structures of Na adsorbates on GaAs(110) observed from STM experiments [12]. The open structure has each Na atom occupying a next-nearest bridge site encompassing a Ga surface atom and two As surface atoms. Our calculated equilibrium geometry for two K atoms on GaAs(110) also displays the same structure, with the K–K distance being 8.02 Å, compatible with the value of 8 Å for the Na–Na distance observed by STM [12].

In this paper, we present our results for the diffusion of an isolated K atom on perfect and stepped GaAs(110) surfaces as well as the preferred geometry for two K atoms on these surfaces. We choose to study K on these two types of GaAs(110) surface partly because it is mostly studied on Si surfaces [13–15]. Also, we wish to investigate whether the stepped surface may promote the clustering of alkali-metal atoms compared to the formation of the more open one- and two-dimensional chain structures at low coverage observed so far from STM experiments. Moreover, most theoretical calculations for alkali-metal adsorbates on GaAs(110) [4–6, 11, 16, 17] tend to focus only on the perfect surface. Presently, we will show that our results for the perfect GaAs(110) surface are compatible with recent STM results for Na on GaAs(110) [12] discussed above as well as other theoretical calculations for alkali metals on GaAs(110) [16, 17]. In addition, the stepped surface does not seem to enhance the clustering of K atoms.

2. Methodology

We use a semi-empirical self-consistent molecular orbital method: the complete neglect of

differential overlap (CNDO) method [18] to investigate the diffusion of K on the GaAs(110) surface. It has been used to investigate the diffusion of self-interstitials in Si [19,20] and Ge [21] via the Bourgoin–Corbett mechanism [22], H-induced passivation of p-type [23] and n-type Si [24] as well as GaAs(110): Be (acceptor) systems [25]. The CNDO parameters for GaAs, which have been reported elsewhere [25], yield calculated values of its bulk properties in good agreement with experimental data, and have also been used in the investigation of H in GaAs [25]. We implement the MOSES code [26] and we perform our calculations on 84-atom (110) ideal and step surface clusters [27,28] to simulate the GaAs(110) surface, which we have previously used to study DIET (desorption induced by electronic transitions) processes and multi-hole localization on GaP(110) surfaces [27–31] and for which details have been given.

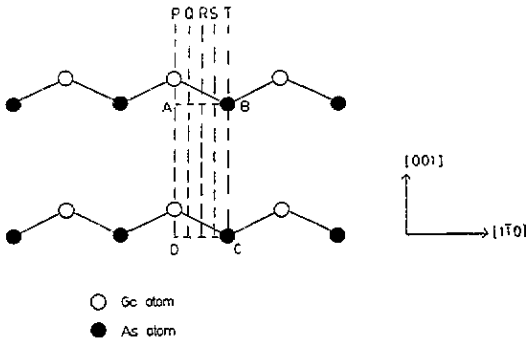


Figure 2. Total energy calculations are performed for the K atoms at 40 different points along the five traverses, P, Q, R, S and T, within the rectangular grid ABCD. By repeating the values of the minimum energy at each point within ABCD along the whole surface, the total energy surface for K on perfect GaAs(110) is obtained as shown in figure 3.

We assume an ideal unrelaxed GaAs(110) surface since surface EXAFS [32,33] and photoemission [34] experiments indicate that the GaAs(110) surface does not relax at low Na (or K) coverage. There is also theoretical [16,35] evidence that the underlying reconstruction is removed upon adsorption of the metal atom. To investigate the diffusion of K on GaAs(110), the K atom is placed at over 40 adsorption sites along each of the five traverses, P, Q, R, S and T, indicated in figure 2. For each site, the K atom is displaced perpendicular to the GaAs(110) surface to obtain the minimum energy position. By repeating the results obtained along the surface, the total energy surface for K on GaAs(110) can then be plotted. This procedure is also repeated for K around a step site.

3. Results and discussion

The results we obtain for the total energy surface of a K atom on a perfect GaAs(110) surface, as calculated above, are illustrated in figure 3. From the contours, the total energy surface has a deep channel, zigzag in nature, and also parallel to the surface zigzag atomic chains. Hence, the nature of K diffusion on GaAs(110) is highly anisotropic and is similar to that of Na on GaAs(110) [16]. Experimentally, the stable atomic adsorption site of K on GaAs(110) is not known although it is highly appropriate to compare our findings with those from the STM observations of Na on GaAs(110) [12]. Our results yield the threefold bridge site as shown on figure 1 as the minimum-energy site, close to a Ga surface atom and two As surface atoms on a neighbouring zigzag chain. At this position, the K–Ga bondlength is 2.53 Å, slightly greater than the bulk bondlength of GaAs (2.45 Å). Also, the K adatom at this site is located at a height of 0.73 Å above the surface plane. The

energy of K at this site is lower than that at a site along the dangling-bond direction of a surface As site by 0.32 eV. Thus, our findings here for the preferred adsorption site of K on GaAs(110) are consistent with the results from other theoretical calculations [4–6, 16, 17] as well as those from experiments [1, 8, 9] for other metals. Of more relevance, our findings are also compatible with the calculations [16] and STM results [12] for Na on the GaAs(110) surface. Along the deep channel, the barrier to diffusion from one bridge site to another is 0.38 eV, while across the surface zigzag atomic chain, the barrier is about 4.7 eV, reflecting the highly anisotropic nature of K diffusion. This result also supports the formation of one-dimensional linear chains in the region between the surface atomic zigzag chains as observed experimentally.

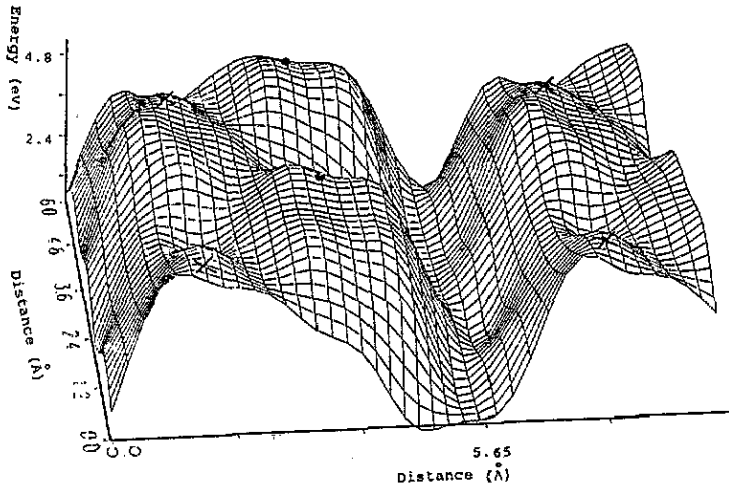


Figure 3. Total energy surface for the K/GaAs(110) system. The crosses mark the location of the surface Ga atoms while the filled circles represent the surface As atoms. Notice the highly anisotropic nature of the diffusion of K in the low-energy channel region between the surface atomic zigzag chains.

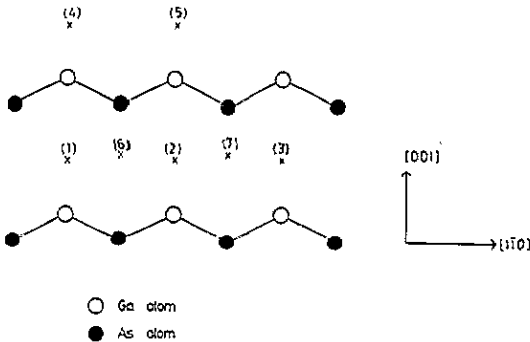


Figure 4. Total energy calculations are performed for different configurations of two K atoms on the perfect GaAs(110) surface. The K atoms are sited at (a) 1 and 2, (b) 2 and 6, (c) 1 and 3, (d) 1 and 4, (e) 1 and 5 (zigzag configuration) and (f) 1 and 7. The global minimum configuration for two K atoms on GaAs(110) is that of (c), with the K atoms occupying sites 1 and 3 (the bridge sites encompassing a surface Ga atom and two As atoms, with a vacant bridge site (2) between them). This is similar to the STM results for Na on GaAs(110) (see figure 1).

Additional calculations are performed for two K atoms on GaAs(110) at various pairs of sites on the same and neighbouring surface atomic zigzag chains as shown in figure 4. Our results show that the two K atoms adsorbed on sites 1 and 3, representing the threefold

bridge sites as in figure 1, in the region between the same pair of surface atomic zigzag chains, display the lowest energy configuration. In this stable geometry for the diatomic K molecule, both the K atoms on the bridge sites in the channel region are separated by an unoccupied bridge site, between the same pair of surface atomic zigzag chains, as observed experimentally [12] for Na. Also, the distance between the two K adatoms is 8.02 Å, compatible with the STM results [12] for Na on GaAs(110) where the Na–Na distance is determined to be 8 Å. This is not surprising in view of the anisotropic nature of K diffusion on GaAs(110) between the atomic zigzag chains of the surface. Thus, the formation of one-dimensional linear adsorbate chains is preferred to two-dimensional islands. Na on GaAs(110) also favours the formation of one-dimensional chains as evident from theory [16] and experiment [12]. The large K–K distance suggests some form of adsorbate–adsorbate repulsion, which is supported by some charge transfer between K and the surface from examination of the Mulliken charge densities, which indicate some loss of charge from the K adsorbates, making them slightly positively charged. The net repulsion between them may prevent them from clustering, thus giving rise to a more open linear chain structure (figure 1) rather than a close-packed one. Also, no charge transfer occurs between the two K adatoms themselves in their equilibrium configuration on GaAs(110) because they possess the same charge. Thus, the negative- U behaviour suggested by Allan and Lannoo [11] for adatom pairing does not appear to hold for K on GaAs(110), although for other metals it may still apply.

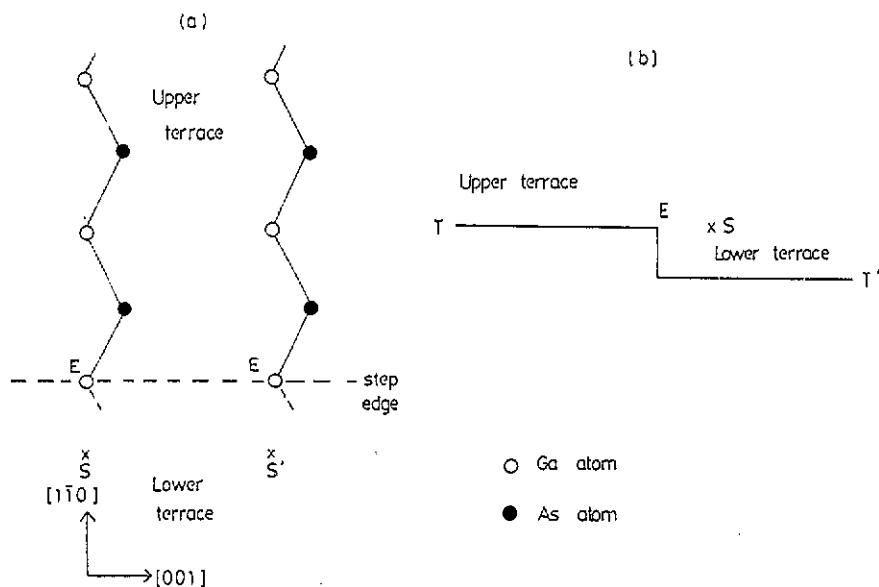


Figure 5. (a) Top view of a stepped GaAs(110) surface with the step edge perpendicular to the surface atomic zigzag chain in the [110] direction. The surface Ga atoms at the edge are represented by E. (b) Side view of the stepped GaAs(110) surface to illustrate the lower and upper terraces. The lower terrace is obtained by removing all the surface atoms of the perfect surface from the step edge onwards, exposing the atoms in the second layer of the original perfect surface. Site S represents the equilibrium site of the K adsorbate on the stepped surface.

Complementary studies to investigate whether the nature of the surface, e.g. stepped, may enhance the likelihood of clustering of alkali atoms are then carried out on an isolated

K atom as well as a pair of K atoms on a stepped GaAs(110) surface. A step is simulated along the (100) direction where the surface atomic zigzag chains are abruptly terminated (see figure 5). This results in an upper terrace which represents the ideal surface before termination of the zigzag chains, and a lower terrace after removal of the first layer of the surface atoms, from the step onwards (see cross-sectional view of surface in figure 5(b)). Repeating the calculations as for the perfect surface with an isolated K atom at various points along several traverses, both on the upper and lower terraces as shown in figure 6, the equilibrium geometry for a K atom on a stepped GaAs(110) surface is determined to be site S as shown in figure 5. This site is lower in energy than the equilibrium bridge site for the perfect GaAs(110) surface by 0.82 eV, indicating that a step appears to enhance adsorption of metal adsorbates. The K-Ga distance for K at site S is calculated to be 2.48 Å, slightly smaller than at the bridge site on the perfect surface. Also, the K atom is located at a height of 0.59 Å above the lower terrace.

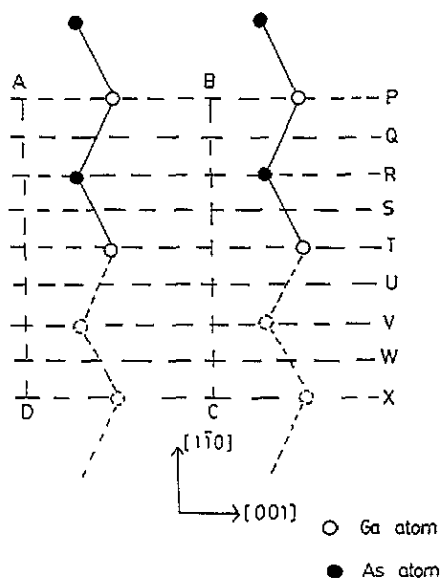


Figure 6. Schematic representation of calculations of total energies to determine the diffusion profile of K on a stepped GaAs(110) surface. Their values are calculated at over 70 points within the rectangular grid ABCD along the nine traverses P, Q, R, S, T, U, V, W and X, covering part of both the upper and lower terraces near the step edge represented by T.

The nature of the diffusion of a K atom around a step edge is also illustrated in figure 7. On the upper terrace before reaching the step edge, the diffusion of the K atom is essentially the same as in figure 3 for the perfect surface, i.e., it diffuses anisotropically between the surface atomic zigzag chains until it reaches the step edge. At the edge, it migrates sideways to a site S above the lower terrace, along the axis of the surface Ga atoms lying on the zigzag chains (see figure 5). When a second K atom is introduced over the stepped surface, it adsorbs at a neighbouring equivalent site S', about 6 Å away from site S, in the equilibrium configuration. This implies that clustering of K atoms at a step is unlikely to occur and may account for the non-observation of K clusters on semiconductor surfaces at low coverage so far. However, the second K atom on the stepped surface (figure 5) is bound more strongly than that on the perfect surface (figure 4) by 1.14 eV, suggesting that formation of one-dimensional chains of metal atoms can also occur and is also more encouraged at stepped surfaces. However, the alignment of the linear chain is more influenced by the orientation of the step, which in this case is perpendicular to the (110) chain on the perfect surface

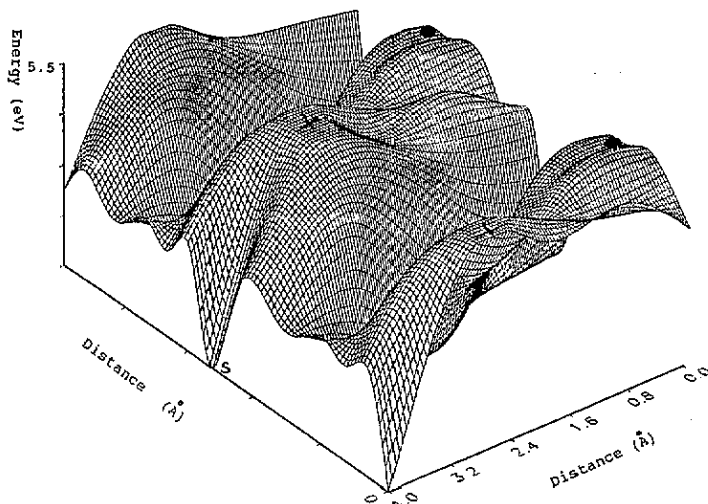


Figure 7. The total energy surface for K around the vicinity of a step edge for K on a stepped GaAs(110) surface. The lowest point represents site S in figure 5. The crosses mark the sites of the surface Ga atoms while the filled circles represent the As atoms.

(see figure 1). Examination of the Mulliken charge densities indicates that there is a slight charge transfer between the surface and K adsorbates, but not between the K adsorbates themselves. Thus, similarly to the situation for the perfect surface, the two K adsorbates do not interact strongly to cluster together.

4. Conclusion

We have simulated the adsorption of monatomic and diatomic K on both perfect and stepped GaAs(110) surfaces. The highly anisotropic diffusion profile of K on the perfect GaAs(110) surface explains why there is a preference to form one-dimensional chains rather than two-dimensional ones. In addition, the equilibrium site for K on GaAs(110) is similar to that for Na on GaAs(110) determined from STM experiments [12]. Thus, our results are consistent with recent theoretical [16] and experimental [12] findings for Na on GaAs(110). The more open structure of the one-dimensional adsorbate chain, supported by the large K–K and Na–Na nearest-neighbour distances determined here (about 8 Å) and experimentally [12], suggests that some form of adsorbate–adsorbate interaction inhibits a closer-packed formation. On the other hand, a K atom appears to adsorb more strongly at a step site and even a second K atom is likewise adsorbed more strongly compared to the same cases on the perfect surface. Like the case for the two K atoms on the perfect GaAs(110) which have practically the same charge, the two K atoms on the stepped surface also display similar charges, suggesting some partial ionic interaction between the two K adsorbates on the stepped surface which prevents them from clustering as well. Hence, it appears that clustering of alkali-metal atoms such as K on semiconductor surfaces is unlikely to be assisted by the presence of steps, but rather, the formation of the one-dimensional adsorbate chain on the stepped surface may be influenced by the orientation of the steps.

References

- [1] Feenstra R M 1989 *Phys. Rev. Lett.* **63** 1412
- [2] First P N, Stroschio J A, Dragoset R A, Pierce D T and Celotta R J 1989 *Phys. Rev. Lett.* **63** 1416
- [3] Krauss M and Stevens W J 1990 *J. Chem. Phys.* **93** 8915
- [4] Ortega J and Flores F 1989 *Phys. Rev. Lett.* **63** 2500
- [5] Klepeis J E and Harrison W A 1989 *Phys. Rev. B* **40** 5810
- [6] Fong C Y, Yang L H and Batra I P 1989 *Phys. Rev. B* **40** 6120
- [7] DiNardo N J, Maeda Wong T and Plummer E W 1990 *Phys. Rev. Lett.* **65** 2177
- [8] Whitman L J, Stroschio J A, Dragoset R A and Celotta R J 1991 *Phys. Rev. Lett.* **66** 1338
- [9] Trafas B M, Hill D M, Siefert R L and Weaver J H 1990 *Phys. Rev. B* **42** 3231
- [10] Patrin J C, Li Y Z and Weaver J H 1992 *Phys. Rev. B* **45** 1756
- [11] Allan G and Lannoo M 1991 *Phys. Rev. Lett.* **66** 1209
- [12] Bai C, Hashizume T, Jeon D R and Sakurai T 1992 *Japan. J. Appl. Phys.* **31** L1117
- [13] Ong C K 1990 *J. Phys.: Condens. Matter* **2** 6731
- [14] Ye Ling, Freeman A J and Delley B 1989 *Phys. Rev. B* **39** 10144
- [15] Kendelewicz T, Soukiassian P, List R S, Woicik J C, Pianetta P, Lindan I and Spicer W E 1988 *Phys. Rev. B* **37** 7115
- [16] Hebenstreit J, Heinemann M and Scheffler M 1991 *Phys. Rev. Lett.* **67** 1031
- [17] Pankratov O and Scheffler M 1993 *Phys. Rev. Lett.* **70** 351
- [18] Pople J A and Beveridge D L 1970 *Approximate Molecular Orbital Theory* (New York: McGraw-Hill)
- [19] Masri P, Harker A H and Stoneham A M 1983 *J. Phys. C: Solid State Phys.* **16** L613
- [20] Khoo G S and Ong C K 1987 *J. Phys. C: Solid State Phys.* **20** 5037
- [21] Khoo G S and Ong C K 1990 *J. Phys. Chem. Solids* **51** 1177
- [22] Bourgoin J C and Corbett J W 1972 *Phys. Lett.* **38A** 135
- [23] Ong C K and Khoo G S 1991 *J. Phys.: Condens. Matter* **3** 675
- [24] Khoo G S and Ong C K 1991 *J. Phys.: Condens. Matter* **3** 6321
- [25] Khoo G S and Ong C K 1993 *Phys. Rev. B* **47** 16369
- [26] Harker A H and Lyon S B 1979 *AERE Harwell Report* R8598
- [27] Ong C K, Khoo G S, Hattori K, Nakai Y and Itoh N 1991 *Surf. Sci.* **259** L787
- [28] Itoh N, Hattori K, Nakai Y, Kanasaki J, Okano A, Ong C K and Khoo G S 1992 *Appl. Phys. Lett.* **60** 3271
- [29] Khoo G S, Ong C K and Itoh N 1993 *Phys. Rev. B* **47** 2031
- [30] Khoo G S, Ong C K and Itoh N 1993 *J. Phys.: Condens. Matter* **5** 1187
- [31] Khoo G S and Ong C K 1993 *Phys. Rev. B* **47** 9346
- [32] Duke C B, Paton A, Meyer R J, Brillson L J, Kahn A, Kanani D, Carelli J, Yeh J L, Margaritondo G and Katani A D 1981 *Phys. Rev. Lett.* **46** 440
- [33] Soukiassian P and Kendelewicz T 1989 *Metallization and Metal-Semiconductor Interfaces* ed I P Batra (New York: Plenum) p 465
- [34] Prietsch M, Labschat C, Domke M and Kaindl G 1988 *Europhys. Lett.* **6** 451
- [35] Zhang S B, Cohen M L and Louie S G 1986 *Phys. Rev. B* **34** 768