Insulating behavior of alkali-metal-covered GaAs(110)

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A combined effort of local density approximation (LDA) and many-body calculations is aimed at an understanding of the nature of the insulating behavior of GaAs(110) under submonolayer alkali-metal coverage. In particular, a Hubbard model is constructed with its parameters extracted from LDA pseudopotential calculations. The electron hopping spectrum is calculated using an exact diagonalization technique. The combined LDA and many-body results demonstrate that the GaAs(110) under submonolayer alkali-metal coverage up to $\theta=0.25$ is a Mott-Hubbard insulator. [S0163-1829(96)00144-0]

The study of alkali metals adsorbed on the GaAs(110) surface has attracted considerable attention.[1] The GaAs(110) surface is one of the best studied semiconductor surfaces and alkali metal represents the simplest metal. The system serves as a prototype in the study of the formation of Schottky barriers.[2] The clean GaAs(110) surface exhibits a simple relaxation pattern which is mainly a rotation of the surface Ga−As chain by about 27 degrees. The surface Ga moves out 0.46 Å and As moves in 0.14 Å.[3] Under low coverage, the adsorbed alkali-metal atom is located about halfway between the Ga atoms along the (001) direction (see Fig. 1). The ideal GaAs(110) surface has a high density of surface electronic states consisting of the dangling bonds of surface atoms.[4] The surface valence (conduction) band has a large component of the As (Ga) dangling bonds. For the ideal surface, the two bands situate in the middle of the bulk gap with a gap between them around 0.3 eV. With relaxation, the gap widens and the surface conduction band dispersion increases from 0.4 eV to 1.4 eV along the surface Ga−As chain direction. Under low alkali-metal coverage, local density approximation (LDA) calculations[3] show that the conduction bandwidth remains large, and that the alkali-metal band stays above the conduction band (see Fig. 2). So the simple band picture suggests that with the alkali-metal atoms donating the electron to the surface conduction band, the surface is a conductor. However, several experiments[5–8] have shown that at submonolayer coverage up to $\theta=0.25$ (corresponding to 0.5 alkali-metal atom per surface unit cell), the surface remains an insulator. Especially the scanning tunneling microscopy (STM) measurement,[6] which directly measures the energy difference between injecting and extracting an electron from the surface, has clearly indicated a gap of 1.1 eV at low coverage, and about 0.65 eV at $\theta=0.25$ coverage.

It was suggested earlier[9] that the GaAs substrate locks the alkali-metal atoms at a distance too big to form a metallic bond, so the surface is a Mott-Hubbard insulator. Later it was found[10] that the surface conduction band character is the dangling bond of Ga instead of the alkali-metal *s* orbit, while the Hubbard model description of the surface remains valid. It was also speculated[11] that alkali-metal coverage may remove the surface relaxation and cause a narrowing of the bandwidth in favor of a Mott-Hubbard insulator. Earlier cal-

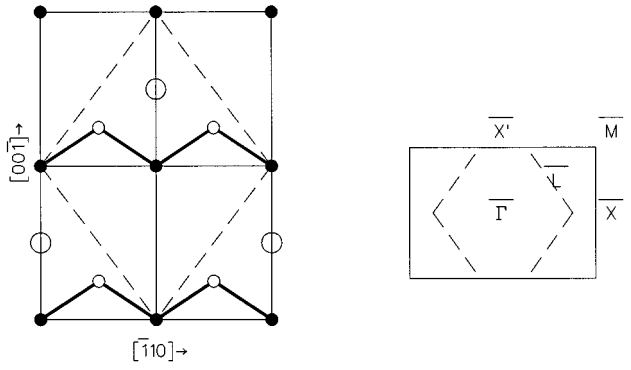

FIG. 1. The GaAs(110) surface and surface Brillouin zone. Filled and open circles denote Ga and As atoms, respectively. The large open circles denote the alkali-metal atoms. The $c(2\times2)$ cell is outlined with dashed lines. The (1×1) Brillouin zone is shown with solid lines, and the $c(2\times2)$ zone is shown with dashed lines. For the $c(2\times2)$, $\bar{M}$ is equivalent to $\bar{\Gamma}$.

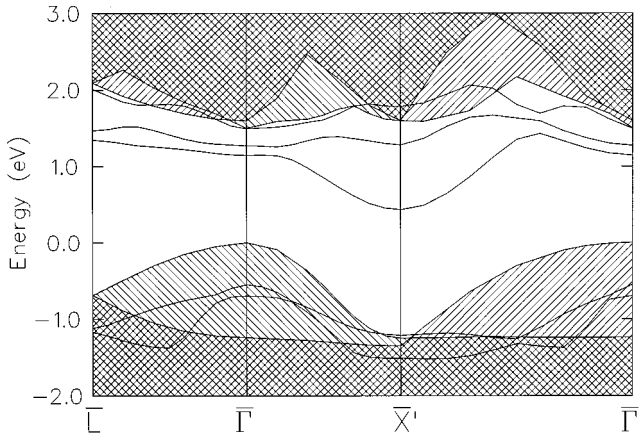

FIG. 2. The band structure of the relaxed $c(2\times2)$ Cs/GaAs(110) surface. Shaded areas are bulk band continuum.

culations have indeed shown[11] that the surface relaxation is lifted under a high coverage of $\theta=1.0$. However, recent calculations have concluded[3,10] that under low coverage of $\theta=0.25$, especially with the large Cs atom, the surface relaxation mostly remains the same as the clean surface.

Of crucial importance to the understanding of the insulating behavior of the alkali-metal covered GaAs(110) is an accurate evaluation of the Coulomb interactions in the system. Earlier estimates of the on-site U were in the range of 0.9–1.8 eV.[10] Since the surface conduction bandwidth is on the order of 1 eV,[3,10] it seems to support the Mott-Hubbard interpretation. However, a recent calculation[12] has reported a much smaller value of 0.56 eV for the U parameter, therefore casting doubt on the validity of the Mott-Hubbard description. A bipolaron model[12] was proposed as an alternative mechanism for the insulating behavior.

In this paper, we report a combined effort of density functional calculations that lead to a *consistent* set of parameters for a Hubbard model and many-body calculations that demonstrate that up to $\theta=0.25$ alkali-metal coverage the GaAs(110) surface is indeed a Mott-Hubbard insulator. The main conclusions are the importance of the consistency of the parameter set and that the intersite Coulomb interactions must be explicitly considered for this system to validate a Mott-Hubbard description. The computational approach devised in this work should be applicable to strongly correlated narrow-band real materials in general.

Our LDA studies on the surface structure and electronic structure of clean and alkali-metal covered GaAs(110) were reported earlier.[3] In this work, we perform self-consistent total energy calculations under various schemes of addition or removal of electrons from the surface conduction bands, and from these total energies extract a consistent set of parameters for the Hubbard model. The structure of fully relaxed GaAs(110) surface under $\theta=0.25$ Cs coverage is used throughout. The surface is modeled by a four-layer slab with hydrogen capping on one side. The positions of hydrogen are optimized to restore a bulklike potential inside the slab. This optimized capping enables us to obtain a well converged surface band and surface relaxation structure that are in good agreement with calculations using thicker slabs.[3] Norm-conserving pseudopotentials[13] with a total charge exchange-correlation scheme[14] are used for Ga, As, and Cs atoms. The electronic wave functions are expanded using about 1400 plane waves with a kinetic energy cutoff of 6 Ry. A regular 8×4 grid mesh in the full (1×1) Brillouin zone is used for the self-consistent calculations.

It is known from LDA calculations that the surface conduction band is highly localized on the surface layer Ga. Therefore we model the surface with a 2D rectangular lattice of the Ga sites. Our model concentrates on the dangling bonds of Ga, so there is only one orbit per atom. With the adsorption of alkali-metal atoms, the surface periodicity changes, so we consider two inequivalent Ga atoms, with Ga* denoting the Ga atom that has an alkali-metal atom at its tetrahedral bond direction. The model for this system thus is a 2D Hubbard model defined by the following Hamiltonian:

TABLE I. The single-particle and interaction parameters for Hamiltonian (1), all in units of eV. The symbols are explained in the text.

t_1	0.17	U^*	1.5
t_2	−0.072	U	1.5
t_3	0.049	K	0.61
Δ	0.10		

$$H=\Delta\sum_{i\in Ga;\sigma} c_{i\sigma}^{\dagger}c_{i\sigma}+\sum_{ij;\sigma} t_{ij}c_{i\sigma}^{\dagger}c_{j\sigma}+\frac{1}{2}\sum_{i\sigma} U_i c_{i\sigma}^{\dagger}c_{i\sigma}c_{i-\sigma}^{\dagger}c_{i-\sigma}$$
$$+\sum_{\langle ij\rangle;\sigma\sigma'} K_{ij}c_{i\sigma}^{\dagger}c_{i\sigma}c_{j\sigma'}^{\dagger}c_{j\sigma'}. \quad (1)$$

Here Δ is the on-site energy difference between the Ga and Ga* sites. We consider three neighboring hopping terms: t_1 between Ga and Ga* along the surface Ga−As chain, t_2 perpendicular to the chain, and t_3 along the diagonal of the surface rectangular lattice. Our LDA calculations show[3] that the relaxation of Ga and that of Ga* are almost identical. This is due to the highly ionic bonding between Cs and GaAs(110) surface. It is also expected that the hopping term t_3 between Ga and that between Ga* are similar. In addition, we consider two intrasite Coulomb interaction terms with parameters U and U^*, and one nearest neighbor intersite interaction term K along the surface chain.

The hopping terms in the model Hamiltonian are determined through a fit of the LDA band structure to a tight-binding model. Under the $c(2\times2)$ symmetry, the eigenvalues for the two surface conduction bands are

$$\epsilon_k^{\pm}=\frac{\Delta}{2}+4t_3\cos\left(\frac{a}{\sqrt{2}}k_x\right)\cos(ak_y)\pm\left\{\left(\frac{\Delta}{2}\right)^2+4\left[t_1\cos\left(\frac{a}{\sqrt{2}}k_x\right)+t_2\cos(ak_y)\right]^2\right\}^{1/2}, \quad (2)$$

where a is the lattice constant of GaAs, and the plus (minus) sign gives the up (lower) conduction band. As mentioned above, we have set $t_3(\mathrm{Ga})=t_3(\mathrm{Ga}^*)$. The four parameters, Δ, t_1, t_2, and t_3, are determined through a least square fit to the LDA band gaps at $\bar{\Gamma}$, X', and L, as well as bandwidths along the chain, perpendicular to the chain, and from $\bar{\Gamma}$ to L. The results are listed in Table I.

We determine the interaction parameters by mapping the LDA total energy under various electron occupation schemes onto the mean-field solution of the Hubbard Hamiltonian.[15] In particular, we concentrate on the part of the LDA total energy that is quadratic in occupation numbers and compare to the corresponding part in the Hubbard model.[16] To obtain nearest neighbor intersite K parameter, it is necessary to use wave functions whose density is localized on either Ga or Ga*. It is easy to see that a linear combination of plane waves $\exp[i(\mathbf{G}/4)\mathbf{r}]\pm\exp[-i(\mathbf{G}/4)\mathbf{r}]$, with $\mathbf{G}$ being the reciprocal lattice vector, will produce standing waves with wavelength $8\pi/|\mathbf{G}|$. The charge density will then have periodicity $4\pi/|\mathbf{G}|$, concentrating on next-nearest neighbor atoms. For the $c(2\times2)$ symmetry, the $\mathbf{G}$ is just

$2\pi(\sqrt{2}/a,1/a)$. As was done before,[12] a single k-point $L=\mathbf{G}/4=\pi/2(\sqrt{2}/a,1/a)$ is used for the surface conduction band, while a regular 8×4 grid of k points in the full (1×1) Brillouin zone is used for bulk bands and surface valence bands. There are two degenerate states at this k point for the clean surface. The degeneracy is lifted once unequal charges occupy the two states, such as under a $\theta=0.25$ alkali-metal coverage.

The evaluation of the interaction parameters involves calculations of total energies under various occupation schemes. In most cases, total energies at four different occupation numbers are calculated for each occupation scheme. The energies are then fitted with a second order polynomial. The coefficient of the second order is directly related to quadratic energy terms in the mean-field solution of the Hubbard Hamiltonian.

Three occupation schemes are used for total energy calculations. The first scheme adds electrons to surface Ga. As can be seen from Hamiltonian (1), the energy term which is quadratic in occupation number is just $\frac{1}{2}U$. The second adds holes to Ga*, the results give $\frac{1}{2}U^*$. The third scheme adds electrons equally to both Ga and Ga* atoms. Here the quadratic energy term is $\frac{1}{2}U+\frac{1}{2}U^*+2K$. The factor of 2 is because there are two Ga−Ga* nearest bond in the $c(2\times2)$ unit cell. For the above three occupation schemes, system charge neutrality is restored by a uniform charge background. The three interaction parameters in Hamiltonian (1) are determined with these three sets of LDA calculations. The results are presented in Table I. The difference between U and U^* is less than 0.1 eV, which shows that the influence of alkali-metal overlayer on the interaction parameters is minor.

To check the consistency of the parameters obtained above, a fourth set of energies are calculated with a different electron occupation scheme where electrons are transferred between Ga and Ga* atoms. The energy term for this charge transfer is $\frac{1}{2}U+\frac{1}{2}U^*-2K$. Here the minus sign is due to the fact that electrons are added to Ga while holes are added to Ga*. Using the parameters in Table I, one gets 0.28 eV for this energy term, while a fit of the fourth set with a polynomial gives 0.32 eV. This clearly shows the consistency of our Coulomb interaction parameters. Notice that should we neglect the intersite K in the Hubbard Hamiltonian, the energy term would be just $\frac{1}{2}U+\frac{1}{2}U^*$. The same fourth occupation scheme would lead to a U of only 0.3 eV, five times smaller than the U obtained from the first and second occupation schemes. Notice further that without including the intersite K, a recent LDA calculation[12] has obtained a U of 0.56 eV.

It should be mentioned that using a single k point for the surface conduction bands introduces a perfect nesting condition for the two-dimensional Fermi surface, hence the electron-phonon interaction and the lattice instability towards a 2×2 superstructure are artificially enhanced. For our calculation, however, this shall not cause a large error because the surface is fixed at the equilibrium structure under Cs coverage. Notice also that a unit cell containing two GaAs units is necessary to obtain intersite parameter K. However, the choice of $c(2\times2)$ unit cell and the k point at L is by no means unique. We have also performed calculations on a $p(2\times1)$ structure and extracted Coulomb parameters for the clean surface. There, the relevant $\mathbf{G}$ is $2\pi(\sqrt{2}/a,0)$, and the special k point is 0.5. The U and K obtained there are consistent with the results reported in Table I.

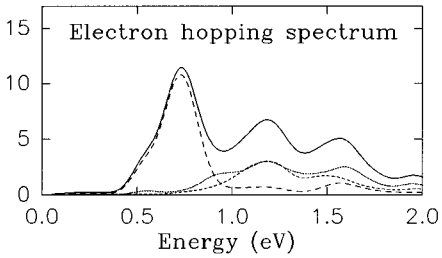

FIG. 3. The calculated electron hopping spectrum through various channels. Long dash: t_1 hopping; medium dash: t_2 hopping; short dash: t_3 hopping; solid line: total hopping spectrum. The discrete spikes in the calculated spectrum, which are characteristic of finite-cluster calculations, are Gaussian broadened with a 0.1 eV half width.

As can be seen from Table I, the large values of the interaction parameters, and the resulting large interaction-to-bandwidth ratio strongly indicate that the insulating behavior in GaAs(110) under submonolayer alkali-metal coverage is driven by the strong electron correlation; therefore the system is a Mott-Hubbard insulator. To quantitatively support this conclusion, we have calculated the electron hopping spectrum to examine the transport dynamics in this system. A symmetry projected exact diagonalization scheme[17] is employed in the context of the finite-cluster approach. We consider four electrons in a 4×2 cluster with four Ga and four Ga* as described by Hamiltonian (1). This electron filling factor corresponds to the GaAs(110) with a $\theta=0.25$ coverage of alkali metal. The Hamiltonian is restricted only to the Hilbert space of the paramagnetic $(S=0)$ state, corresponding to the experimental situation of the GaAs(110) system. The electron hopping spectrum is defined as

$$F_{\mathrm{EH}}(\epsilon;\sigma)=\sum_n \sum_{\langle ij\rangle} |\langle \phi_n|c_{i\sigma}^{\dagger}c_{j\sigma}|\phi_0\rangle|^2 \delta(\epsilon+E_n-E_0), \tag{3}$$

where $|\phi_0\rangle$ is the ground state with energy E_0, and $\{|\phi_n\rangle\}$ is the complete set of the eigenstates of the system with energy $\{E_n\}$. The operator $c_{i,\sigma}$ ($c_{i,\sigma}^{\dagger}$) destroys (creates) an electron with spin σ and site index i. The twisted boundary conditions are used to reduce the finite size effect in the calculated results.[18] We have calculated the spectrum with periodic, antiperiodic, and open boundary conditions and the results are then averaged to give the final spectrum.[19] The calculated spectrum is presented in Fig. 3. The results are plotted for various hopping channels. One can clearly see a gap of about 0.6 eV, defined by the midpoint of the rising edge of the first significant peak, in excellent agreement with the experimental STM measurement.[6] The low-energy transport dynamics is dominated by the one-dimensional t_1 channel, i.e., along the Ga−As chain direction. These results strongly support the Mott-Hubbard interpretation for the insulating behavior of alkali-metal covered GaAs(110).

An analysis of the many-body wave function reveals that the intersite Coulomb interaction K is crucial in stabilizing the ground state that essentially has four electrons on the four Ga* sites. The ground state is thus in fact a half-filled Hubbard model for the Ga* sublattice. From this ground state configuration, the energy cost for t_1 hopping is roughly K, while those for t_2 and t_3 hopping are about $2K$ and U. Indeed, three major peaks are observed in the calculated spectrum at these energies with the details modified by the kinetic energy. This analysis demonstrates that the insulating behavior comes naturally in the Mott-Hubbard picture when the intersite interaction is explicitly included and that the insulating ground state does not critically depend on specific values of parameters, as long as U is large enough to prevent double occupancy. The insulating gap is essentially determined by K.

In conclusion, we have obtained a consistent set of parameters for a Hubbard model for the GaAs(110) surface with submonolayer alkali-metal coverage. The parameter set is then used in a many-body calculation of the electron hopping spectrum. The calculation reveals that the intersite interaction, besides being important for the consistency of the parameters, is crucial in the understanding of the insulating ground state. These results unambiguously demonstrate that the GaAs(110) surface under alkali-metal coverage up to $\theta = 0.25$ is a Mott-Hubbard insulator. And the excellent agreement with experiment indicates that our model has captured essential physics of this very interesting system.

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