

# Electronic Surface States

## Nearly-Free Electron Model

In general, the way to find the states of the surface is to solve the Schrödinger equation with the appropriate potentials.

$$\left[ -\frac{\hbar^2}{2m} \frac{d^2}{dz^2} + V(z) \right] \psi(z) = E \psi(z)$$

At the surface, the potential changes suddenly.

$$V(z) = \left[ \exp\left(\frac{2\pi\lambda z}{a}\right) + \exp\left(-\frac{2\pi\lambda z}{a}\right) \right] = 2\hat{V} \cos\left(\frac{2\pi z}{a}\right) \quad (z < 0)$$

$$V(z) = V_0 \quad (z \geq 0)$$

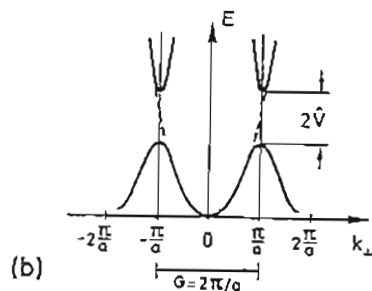
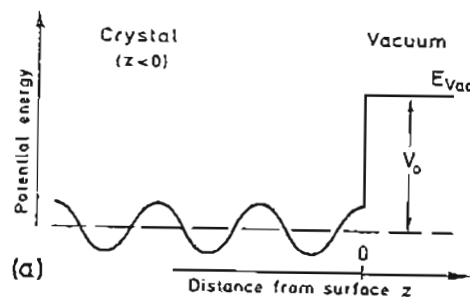


Fig. 6.1a,b. Nearly-free-electron model for a cosine potential along a linear chain ( $z$ -direction). (a) Potential energy in the presence of a surface at  $z = 0$ . (b) Energy bands  $E$  ( $k_{\perp}$ ) for one-electron bulk states

A few more words about the origin of a band gap.  
Based on the free-electron model

The key point is that at the <sup>first</sup> Brillouin zone edge,

$$k = \pm \frac{\pi}{a}$$

The wave function there is a standing wave. It can be

$$\psi(+)=e^{\frac{i\pi z}{a}}+e^{-\frac{i\pi z}{a}}=2\cos\left(\frac{\pi z}{a}\right)$$

$$\text{or } \psi(-)=e^{\frac{i\pi z}{a}}-e^{-\frac{i\pi z}{a}}=2i\sin\left(\frac{\pi z}{a}\right)$$

The probability density is  $\psi^*\psi$

$$\rho_+(z)=\psi^*(+)\psi(+)\propto\cos^2\left(\frac{\pi z}{a}\right)$$

$$\rho_-(z)=\psi^*(-)\psi(-)\propto\sin^2\left(\frac{\pi z}{a}\right)$$

$\rho_+$  piles up electrons near the ion cores

$\rho_-$  piles up electrons in between the ion cores

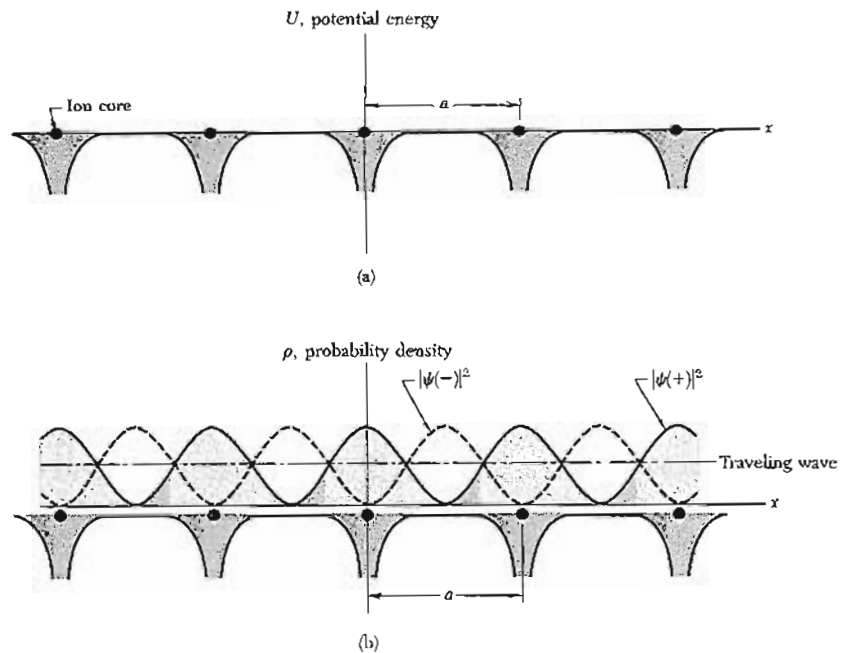


Figure 3 (a) Variation of potential energy of a conduction electron in the field of the ion cores of a linear lattice. (b) Distribution of probability density  $\rho$  in the lattice for  $|\psi(-)|^2 \propto \sin^2 \pi x/a$ ;  $|\psi(+)|^2 \propto \cos^2 \pi x/a$ ; and for a traveling wave. The wavefunction  $\psi(+)$  piles up electronic charge on the cores of the positive ions, thereby lowering the potential energy in comparison with the average potential energy seen by a traveling wave. The wavefunction  $\psi(-)$  piles up charge in the region between the ions, thereby raising the potential energy in comparison with that seen by a traveling wave. This figure is the key to understanding the origin of the energy gap.

Kittel, p. 178  
 "Intro. to Solid State Physics"  
 7th Ed.

The potential can be written:

$$U(x) = U \cos(2\pi x/a) = \underbrace{2 \hat{V} \cos\left(\frac{2\pi x}{a}\right)}_{m \text{ Lith}}$$

The energy gap between  $\psi(+)$  and  $\psi(-)$  is; to first order,

$$E_g = \int_0^a dx U(x) \left[ |\psi(+)|^2 - |\psi(-)|^2 \right]$$

$$E_g = 2 \int_0^a dx U \cos\left(\frac{2\pi x}{a}\right) \left( \cos^2\left(\frac{\pi x}{a}\right) - \sin^2\left(\frac{\pi x}{a}\right) \right) = \underline{\underline{U}}$$

Kittel, p. 179

$$\bar{E} = \frac{\hbar^2}{2m} \left( \frac{\pi}{a} + k \right)^2 \pm |\hat{V}| \left[ \frac{-\hbar^2 \pi k}{m a |\hat{V}|} \pm \sqrt{\left( \frac{\hbar^2 \pi k}{m a |\hat{V}|} \right)^2 + 1} \right]$$

- Lüth, p. 268

with

$$\Psi_{\pm} = C e^{iKz} \left\{ e^{i\pi z/a} + \frac{|\hat{V}|}{\hat{V}} \left[ \frac{-\hbar^2 \pi k}{m a |\hat{V}|} \pm \sqrt{\left( \frac{\hbar^2 \pi k}{m a |\hat{V}|} \right)^2 + 1} \right] e^{-i\pi z/a} \right\}$$

- Lüth, p. 268

These energy and wavefunction solutions are for inside the crystal.

They must be matched at the surface ( $z=0$ ) to an exponentially decaying function

$$\Psi_0 = D \exp\left[-\sqrt{\frac{2m}{\hbar^2}(V_0 - E)} z\right] \quad E < V_0$$

Lüth, p. 268

and  $\Psi_0(z=0) = \alpha \Psi_1(z=0, K) + \beta \Psi_2(z=0, -K)$

Lüth, p. 269

The matching conditions can be fulfilled

at every value of  $\bar{E}$  in the above solution

The result is almost no change in <sup>standing</sup> Bloch waves up to the surface matched to the exponentially decaying tails.

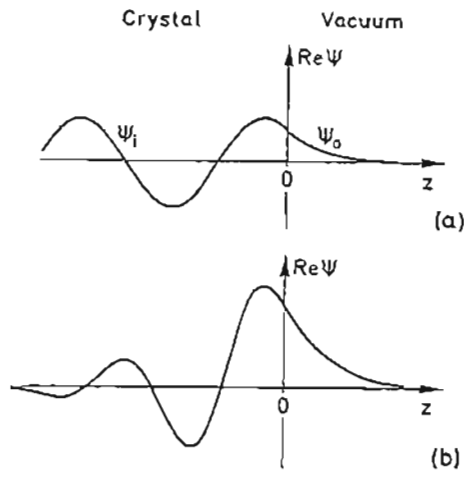


Fig. 6.2. Real part of the one-electron wavefunction,  $\text{Re}\{\psi\}$ , for (a) a standing Bloch wave ( $\psi_1$ ), matched to an exponentially decaying tail ( $\psi_0$ ) in the vacuum; (b) a surface-state wave function localized at the surface ( $z=0$ )

Lüth, p. 269

The top picture is for the bulk-like solution.  
standing Bloch wave matched to decaying exponential.

Consider the energy of the wave for this bulk-like solution

The first part:

$$\frac{\hbar^2}{2m} \left( \frac{\pi}{a} + K \right)^2 = \frac{\hbar^2}{2m} k_{\perp}^2$$

this is just the free-electron like energy (i.e.  $\frac{\hbar^2 k^2}{2m} = KE$ )

Consider the second part

$$\pm |\hat{V}| \left( \frac{-\hbar^2 \pi K}{m a |\hat{V}|} \right) = \mp \frac{\hbar^2}{2m} \left( \frac{2\pi K}{a} \right)$$

this is a small term linear in K

Consider the third part

$$\pm |\hat{V}| \sqrt{\left( \frac{\hbar^2 \pi K}{m a |\hat{V}|} \right)^2 + 1}$$

this part is always  $\geq 1 \Rightarrow$

The above represents the energy of a bulk-like wave.

To find "surface states", we need states which exist only near  $z=0$ ,

Such solutions exist for imaginary wave vectors.

$$K = -ig$$

Actually, we can write the first part and second part together (taking only the - sign part of the second term)

$$\begin{aligned} \frac{\hbar^2}{2m} \left[ \left( \frac{\pi}{a} + K \right)^2 - \left( \frac{2\pi K}{a} \right)^2 \right] &= \frac{\hbar^2}{2m} \left[ \left( \frac{\pi}{a} \right)^2 + K^2 \right] \\ &= \left\{ \frac{\hbar^2}{2m} \left[ \left( \frac{\pi}{a} \right)^2 - g^2 \right] \right\} \end{aligned}$$

This is the first term of Eq. 6.12 in Lüth, p. 269

Considering the third term

$$\pm |V| \sqrt{\left( \frac{\hbar^2 \pi K}{ma|V|} \right)^2 + 1} = \pm |V| \sqrt{1 - \left( \frac{\hbar^2 \pi g}{ma|V|} \right)^2}$$

This part is always less than 1

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Thus, the solutions have imaginary wave vectors will also have an energy split, i.e. there are 2 solutions of energy with a given  $\delta$ , but the energy split is smaller than the energy split for the bulk-like solution with real  $k$ .

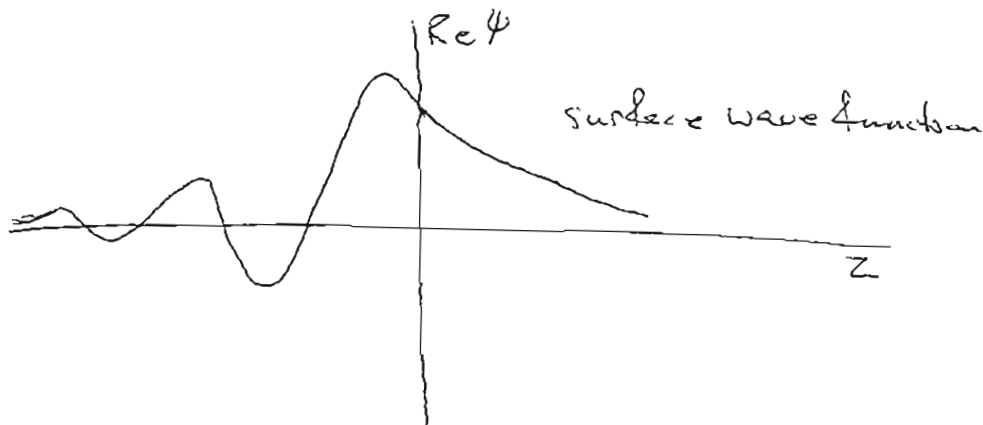
And, this solution corresponds to the surface state  $\psi_i'$  for  $z \leq 0$

$$\psi_i'(z \leq 0) = F e^{\delta z} \left\{ \exp\left[i\left(\frac{\pi}{a}z \pm \delta\right)\right] \mp \exp\left[-i\left(\frac{\pi}{a}z \pm \delta\right)\right] \right\} e^{\mp i\delta}$$

decaying exponential for negative  $z$ 
standing wave
Lieth, p. 269

~~oscillates~~

Thus we have a solution which ~~oscillates~~ <sup>oscillates</sup> like a standing Bloch wave, but it decays into the bulk. Thus, it is a surface wave function corresponding to a surface state. It is also matched to an exponentially decaying function going into the vacuum.



The final result shows that the surface states lie inside the bulk band gap.

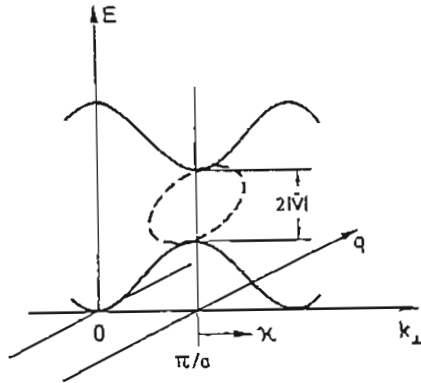


Fig. 6.3. Electronic band structure (qualitative) for a semi-infinite chain of atoms. Bulk Bloch states which are little disturbed by the presence of the surface give rise to energy bands  $E(k_{\perp})$  that are periodic in wave vector  $k_{\perp}$  parallel to the chain direction, i.e. normal to the surface (solid curves). States with a wave function amplitude exponentially decaying from the surface ( $z = 0$ ) into the bulk ( $z < 0$ ) are found between the bulk states for complex wave vectors  $\pi/a - iq$  (broken curve)

Lüth, p. 270

The real case must also take into account the additional  $k_{\parallel}$  allowed at a surface:

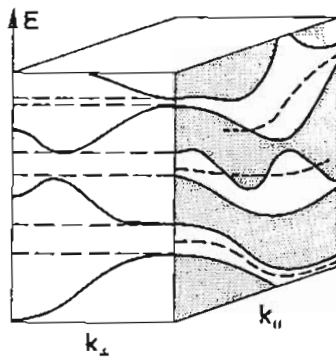


Fig. 6.4. Hypothetical electronic band structure of a crystal. The shaded areas in the  $E(k_{\parallel})$  plane describe the projected bulk-band structure (along  $k_{\perp}$ ). Broken lines in the  $E(k_{\parallel})$  plane indicate surface state bands in the gaps of the projected bulkband structure, and surface resonances where they are degenerate with bulk states (short dotted lines)

Lüth, p. 271

# Example from GaN(0001)

from A.R. Smith et al., *JUSTB* 16(4), 2242 (1998).

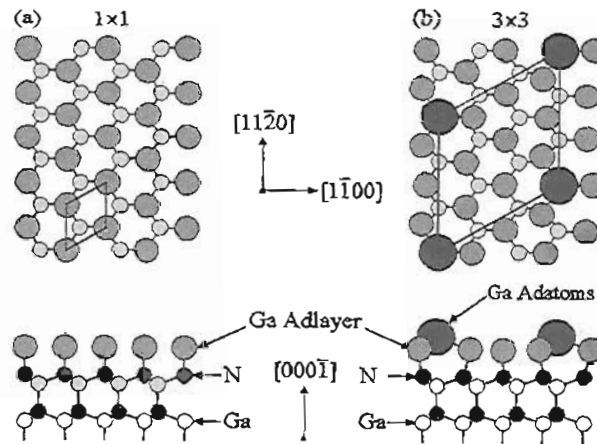


FIG. 1. Model structures determined for the (a)  $1 \times 1$  Ga adlayer structure and (b)  $3 \times 3$  adatom-on-adlayer structure of GaN(0001). The Ga adlayer is under tensile stress since the Ga atoms are stretched further apart compared to their spacing in bulk Ga ( $3.19 \text{ \AA}$  compared  $\sim 2.7 \text{ \AA}$ ). For the  $3 \times 3$  structure, the adlayer atoms are able to get closer together by moving in the in-plane (lateral) direction away from the Ga adatoms by  $0.51 \text{ \AA}$ , thus relieving the stress. All other lateral or vertical displacements of the adlayer atoms are less than  $0.1 \text{ \AA}$ .

Smith et al., p. 2243

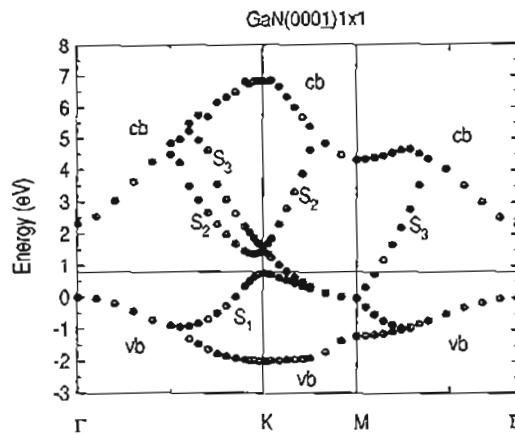


FIG. 2. Band structure for the GaN(0001) $1 \times 1$  Ga adlayer based on local density functional calculations. Energies are plotted relative to the VBM. The Fermi level is located  $0.75 \text{ eV}$  above the VBM. The plot shows the valence and conduction band edges and three surface states:  $S_1$ ,  $S_2$ , and  $S_3$ . The computed bulk band gap of GaN is less than the experimental value ( $3.4 \text{ eV}$ ).

Smith et al., p. 2244

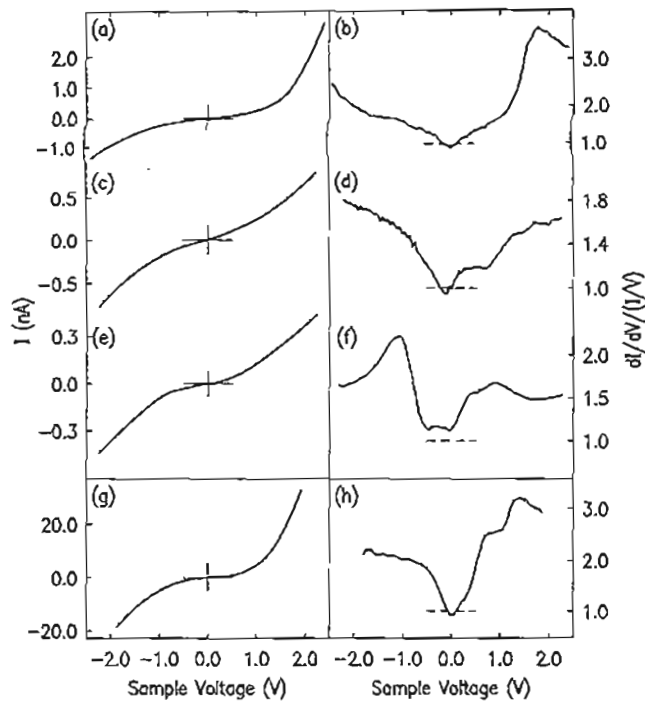


FIG. 5. Averaged tunneling spectroscopy results from three separate experiments (three different tips) on the GaN(0001)  $1 \times 1$  surface (a)–(f) and a single experiment on the GaN(0001) “ $1 \times 1$ ” surface (g) and (h).  $I$ – $V$  curves are shown on the left with the corresponding normalized conductance curves shown on the right. Crossmarks represent the origins for the  $I$ – $V$  curves, while dashed lines indicate where the normalized conductance = 1.

- Smith et. al, p. 2244

Surface states can also be considered from a local, tight-binding picture.

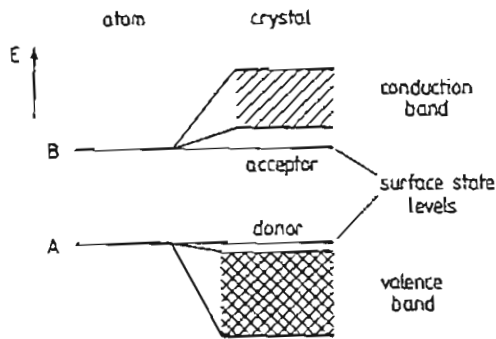


Fig. 6.5. Qualitative explanation of the origin of surface states in the tight-binding picture. Two atomic levels A and B form the bulk valence and conduction bands, respectively. Surface atoms have fewer bonding partners than bulk atoms and thus give rise to electronic energy levels that are closer to those of the free atoms, i.e. surface state levels are split off from the bulk bands. Depending on their origin, these states have acceptor- or donor-like charging character

Lith, p. 273