SURFACE STATES AND ADSORPTION IN AN EXTERNAL ELECTRIC FIELD
M. Stwślicka, M. Radny

To cite this version:
M. Stwślicka, M. Radny. SURFACE STATES AND ADSORPTION IN AN EXTERNAL ELECTRIC FIELD. Journal de Physique Colloques, 1984, 45 (C9), pp.C9-65-C9-70. <10.1051/jphyscol:1984912>. <jpa-00224390>

HAL Id: jpa-00224390
https://hal.archives-ouvertes.fr/jpa-00224390
Submitted on 1 Jan 1984

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
SURFACE STATES AND ADSORPTION IN AN EXTERNAL ELECTRIC FIELD

M. Stęślicka* and M. Radny*

International Centre for Theoretical Physics, Trieste, Italy
*Institute of Experimental Physics, Cybulskiego 36, 50-205 Wrocław, Poland

Resumé - On a établi que les niveaux superficiels créés par les atomes adsorbés, à l'opposé des niveaux de Tamm, sont extrêmement sensibles à la présence d'un champ électrique externe. Le champ électrique positif ne change pas la localisation des niveaux ; tandis que le champ négatif transforme les niveaux créés par les atomes adsorbés et les niveaux de Tamm en niveaux virtuels.

Abstract - It is found that the adsorption-like states contrary to the Tamm-like states are very sensitive to the presence of an external electric field. A positive electric field does not really influence the localization properties of the states; a negative electric field, however, changes the Tamm- and adsorption-like states into virtual states.

INTRODUCTION

In our previous /1/ we have studied the behaviour of surface states in the presence of adsorbed atoms and we have obtained Tamm-like electron localized at the crystal surface and adsorption-like electronic states electron localized near the adatom. Here we investigate the effect of a positive external electric field EEF and of a negative EEF on surface states of a semiinfinite δ-well crystal model with the surface covered by foreign atoms.

MODEL AND NOTATION

The model potential is shown in Fig. 1a (crystal model with positive EEF) and in Fig. 1b (crystal model with negative EEF).

![Diagram](Fig. 1 - Schematic plot of the model potentials V(x) (for notation see the text).)

*Permanent address: Institute of Experimental Physics, Cybulskiego 36, 50-205 Wrocław, Poland.
The electric intensity $F$, (for $0 < x < d$) is assumed to be smaller than $F_0$ (for $x > d$). The presence of an adatom near the crystal surface ($x = 0$) is taken into account via the suitable "modulation" of the surface potential barrier $V_A < V_o$ ($V_o$ being the work function) and the change of the parameter $p$ (the strength of the potential of the adatom) (cf. /1/).

Numerical calculations were carried out with crystal parameters appropriate for silicon, i.e. $V_o = 4.8$ eV, $b = 5.44$ Å, $p = 1.9$. The "internal" field intensity $F$ was taken from the interval $10^6$ V/cm - $10^9$ V/cm (for $F < 10^5$ V/cm the dependence $E = f(d)$ was the same as for $F_0 = 10^5$ V/cm).

**ENERGY EXPRESSIONS AND LOCALIZATION PROPERTIES**

Using the standard matching procedure we have obtained the following expressions for the surface states energy $E$

$$b\sqrt{2E}c_\theta b\sqrt{E} = -\frac{bV_0}{\rho} - b\Delta(\tau)bA_{\eta}(\tau) - \frac{2p}{2\rho}$$

where

$$\Delta(\tau) = \frac{N^2D^+\pm M^2(z_0,z_0)}{M^2(z_0,z_0) + D^+M(z_0,z_0)}$$

with

$$M^+(z_0,z_0) = A'(z_0)B(z_0) - A(z_0)B'(z_0)$$
$$M^-(z_0,z_0) = A(z_0)B(z_0) - A'(z_0)B'(z_0)$$
$$N^2 = A'(z_0)B(z_0) - A(z_0)B'(z_0)$$
$$D^+ = A(z_0)\alpha_1(\hbar^2/2\rho + \beta_2 I^{2})^{-1}$$
$$I^{(z_0,z_0)} = (A'(z_0) - \Theta[A'(z_0),B'(z_0)]xB'(z_0)\times q\beta)$$
$$\Theta[A(x),B(x)] = \begin{cases} 1 & \text{for } x = y \ (y = z_0) \\ 0 & \text{otherwise} \end{cases}$$
$$I^{(z_1,z_2)} = \frac{dH^\pm}{dz}(z_1,z_2)$$
$$\alpha_i = (2F_i)^{1/2} i = 1,2$$

$z_0 = 2(V_o - E)\alpha_i^{-2}$
$z_0 = z_0 \pm d\alpha_i$
$z_\pm = (V_o - E \pm F_\pm d)2\alpha_i^{-2}$
$\beta = \frac{2}{3} |z_0|^{3/2} + \frac{F_0}{4}$
$z_0 = (V_o - E - F_\pm d)2\alpha_i^{-2}$. 


A(z) and B(z) denote Airy functions; "+" "-" sign stands for the positive (negative) EEF, respectively.

The localization properties of an electron occupying the surface states were discussed using the relative probability density function \( P(x) \) defined by \( \frac{\psi(x)^2}{\psi(0)^2} \).

\[
P(x) = \frac{\psi(x)^2}{\psi(0)^2},
\]

where \( \psi(x) \) is the wave function for a surface state (the crystal surface is always located at \( x = 0 \) – see Figs 1a and 1b). Inside the crystal \((-b \leq x \leq 0)\), \( P(x) \) is given by

\[
P_i(x) = \left[ \frac{\cos b \sqrt{2 E} - \sin b \sqrt{2 E} (1 + x/b)}{\sin b \sqrt{2 E}} \right]^2,
\]

where

\[
\gamma = \cos b \sqrt{2 E} - [b \Lambda(\pm) + 2 P] \frac{\sin b \sqrt{2 E}}{b \sqrt{2 E}}.
\]

Outside the crystal for \( 0 \leq x \leq d \), \( P(x) \equiv P_{ii}(x) \) and

\[
P_{ii}(x) = \left[ \frac{M^+ \pm (z^\pm_0, z^\pm_0) \pm D^\pm M^+ \pm (z^\pm_0, z^\pm_0)}{M^- \pm (z^\pm_0, z^\pm_0) \pm D^- M^- \pm (z^\pm_0, z^\pm_0)} \right]^2,
\]

where \( z^\pm = z_o \pm \xi x \). For \( x \geq d \), \( P(x) \equiv P_{iii}(x) \) and is given by

\[
P_{iii}(x) = \left[ \frac{A(z^\pm_0)G}{A(z_\pm_0)H^\pm - \nu K M^+ \pm (z^\pm_0, z^\pm_0)} \right]^2,
\]

where

\[
G = \alpha_2 A(z^\pm_0) H^\pm (z^\pm_0, z^\pm_0),
\]

\[
K = \alpha_4 A(z^\pm_0) \left[ A(z^\pm_0) - A(z^\pm_0) D^\pm \right],
\]

\[
z^\pm_\infty = (V_0 - E \pm F_x) 2 \alpha_2^2.
\]

**NUMERICAL RESULTS**

The effect of an external electric field on both the energy dependence \( E = f(d) \) of the Tamm-like and adsorption-like states and on the relative probability \( P(x) \) can be summarized as follows.

Positive (Fig. 2) and negative EEF's (Fig. 3) change drastically the energy dependence \( E = f(d) \) of the adsorbed-like states (dotted dashed lines for EEF and dashed lines for zero field applied).
The energy of the Tamm-like states (Figs 2 and 3) is almost independent of the field intensities $F_1$ and $F_2$ (dotted lines for EEF and solid lines for zero field applied).

In the model with a negative field the Tamm- and adsorption-like states are replaced by virtual surface states (cf. /3/ and /4/) as can be seen in Fig. 3 (insert for points A and B).

![Diagram](image1)

**Fig. 2 -** $E = f(d)$ for positive EEF (for notation see the text)

The localization properties of the Tamm-like and adsorption-like states are almost not sensitive to the presence of an EEF (Figs 4 and 5). For the negative field, however, $P(x)$ has oscillatory character outside the crystal (Fig. 5), i.e. electrons from virtual states can tunnel through the potential barrier.

![Diagram](image2)

**Fig. 3 -** $E = f(d)$ for the negative EEF (for notation see the text)
**Fig. 4** - $P(x)$ for the positive EEF: a) Tamm-like states, b) Adsorption-like states.

**SUGGESTED INTERPRETATION OF THE RESULTS** based on the Volkenstein of chemisorption /5/

With no electric field applied, the curves $E(d)$ for the adsorption-like and Tamm-like states intersect (see Figs 2 and 3). The ground state has an ionic character (an electron from adatom is tunnelling into empty surface state). There is a possibility of a direct ionic evaporation without a field.

In a strong positive electric field, the "adsorption" curve is strongly deformed and the curves $E(d)$ do not intersect (Fig. 2). Thus the ground state is purely ionic at any distance from the crystal surface. In principle, therefore, an electron of the image gas can tunnel into this state (the corresponding calculations are in progress). For $F \geq 5 \times 10^8$ V/cm, "adsorption" curve merge into the conduction band (no localized states - the case corresponding to the field desorption).

In a negative electric field, the adsorption and Tamm $E(d)$ curves intersect at smaller surface-adatom distance (negative field seems to "push" adatom towards the crystal surface).

We believe that our results might form the starting point for more realistic model of chemisorption involving surface states, thus becoming extension of Volkenstein's theory of chemisorption (see /5/).

**Fig. 5** - $P(x)$ for the negative EEF: a) Tamm-like states, b) Adsorption-like states.
REFERENCES