

Electrotransport on Surfaces and Interfaces *

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A summary of possible mechanisms of surface and interface mass transport in the presence of an electric field and current, and a brief review of experimental data are presented. Emphasis has been given to the relationship between faceting on metal surfaces and a charge carrier flow. A theory for this is presented based on the theory of pure thermal faceting by Mullins⁸. The calculated values of the effective charge show a negative temperature gradient and are close to one for reasonably high temperatures, proving that the "drift term" caused by charge carrier scattering is negligible.

This contribution briefly surveys present knowledge and touches on questions concerning the change of surface and interface mass transfer due to a superimposed electric field and a charge carrier flow.

Although SKAUPY¹ in 1924 and SCHWARZ² in 1939 performed experiments which showed clearly a distinct influence of the electric current on surface mass flow, there is very little quantitative information available on this subject. This is mainly because there is a lack of knowledge of surface properties, particularly of electronic properties. Skaupy observed on tungsten wires what has been called "Gleichstromeffekt". Schwarz observed polonium tracer migration towards the anode on silver wires annealed by DC.

The interaction between the activated migrating surface particle and the field can be due to Coulomb forces by ionization and dipole forces. The interaction with the current carriers must be due to inelastic scattering. The proportionality between the surface mass drift and the diffusion coefficient demonstrates that large effects can be expected compared with the volume, if the surface diffusion coefficient exceeds the volume coefficient by several orders of magnitude. But this cannot be assumed necessarily. There is a large scatter in the experimental data on surface selfdiffusion coefficients. The theory for this, on the basis of the terrace-ledge-kink model and hard spheres interacting with central forces yields values for an undisturbed smooth surface of the same order of magnitude as the vol-

ume. The reason for this is the formation energy for adsorbed atoms on the surface which are in equilibrium with the appropriate number of vacancies in the top atom layer. But if the adsorbed migrating atoms which contribute dominantly to surface diffusion are supplied by other sources, e. g., lattice defects, or from the exterior, the drift velocity is increased since the formation energy can be omitted or reduced. The self-diffusion on high index planes should be expected to be faster than on low index planes since the number of migrating atoms is larger due to a lower enthalpy of formation.

1. Field-microscope

Dipole forces have to be considered only in the field-microscopes as far as the so-called build-up process in a field of several Volts/Å normal to the surface takes place. The induced dipoles lead directly to a reduction in the activation energy of the appropriate surface diffusion process.

DYKE and CHARBONNIER³ cited an equation for the time of the build-up process which can be used to calculate ΔQ with the help of E_0 and an "equilibrium" field strength E_G which does not allow the emitter tip to dull or to facet. The comparison of measured and calculated values according to Dyke and Charbonnier for W, Mo and Nb shows a marked discrepancy which originates from the different geometries in the tip shape conversion during the two different processes.

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¹ F. SKAUPY, Z. Techn. Phys. 5, 563 [1924].

² K. H. SCHWARZ, Z. Elektrochem. 45, 712 [1939].

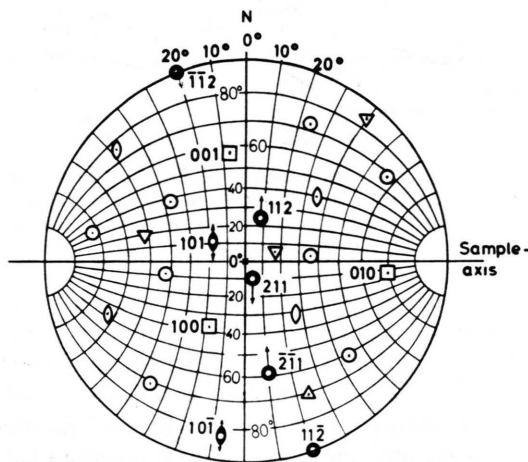
³ W. P. DYKE, F. M. CHARBONNIER et al., J. Appl. Phys. 31, 790 [1960].



As far as second components are migrating over the surface, the permanent dipoles which are interacting with the gradients of the tangential field component may have to be taken into consideration. But the discrepancies of ΔQ_{exp} and ΔQ_{theor} cannot be explained by the tangential field component.

2. Electrotransport and Faceting

the main driving force, the surface free energy, whose orientation dependence under adsorption is usually not known, has to be considered. The essential fact of faceting with electro-transport is the gradual or complete suppression of faceting on one side of a single crystal and an enhanced growth on the other side if the experimental conditions are appropriate. Figure 1 illustrates this fact for a tungsten single crystal.



The growth of linearly extended singular facets can be described with MULLINS' theory⁸. It represents an approximation since the gradient of the surface free energy is taken to be zero. The differential equation for the surface profile $y(x, t)$ takes into account the curvature of the surface as the only driving force as far as faceting is diffusion controlled. But the boundary conditions $x^* = \omega(Bt)^{1/4}$ and $y^* = -n\omega(Bt)^{1/4}$ for the facet parameters x^* , y^* , which are not appropriate to the pure transport differential equation, include implicitly the force $d\gamma/dx$. Otherwise, the facets would not grow. The obtained solutions, therefore, are a first approximation and

in Ulm 1955. — G. M. NEUMANN, Dissertation TU Berlin 1965. — G. M. NEUMANN, W. HIRSCHWALD, and I. N. STRANSKI, Z. Metallkde. **57**, 836 [1966]. — G. M. NEUMANN, W. HIRSCHWALD, and I. N. STRANSKI, J. Phys. Chem. Sol. Suppl. **1**, 619 [1967]. — D. O'BOYLE, J. Appl. Phys. **36**, 2849 [1965]. — R. W. SCHMIDT, Mitteilung der OSRAM-GmbH, Berlin 1942. — D. N. VASILKOVSKY and E. M. TADZHIIEVA, Fiz. Tverd. Tela **4**, 90 [1962].
⁸ W. W. MULLINS, Phil. Mag. **6**, 1313 [1961].

⁷ P. ADAM, Dissertation TU Berlin 1968. — P. ADAM and H. WEVER, *Surface Sci.* **21**, 307 [1970]. — H. J. BOOSS, Dissertation FU Berlin 1965; E. HEINRICH, Dissertation TU Berlin 1953; R. HÖRBE, Dissertation TU Berlin 1960. — R. P. JOHNSON, *Phys. Rev.* **54**, 459 [1939]. — K. KERRER, Vortrag Tagung Phys. Ges. Württemberg-Baden-Pfalz

can be altered with new boundary conditions in the presence of a transport force F_c on high indexed planes and F_s on low indexed planes. The resulting model for faceting with electro-transport is shown in Fig. 2. A rough estimate of the effective charge, on the basis of the results on tungsten yields values

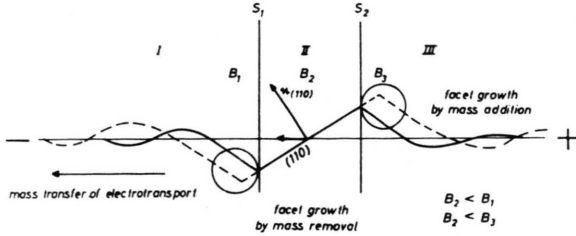


Fig. 2. Schematic representation of enhanced facet growth with electrotransport. The 110-plane is assumed to have a low mobility B_2 for surface diffusion compared with neighbored complex planes⁹.

of $Z^* \cong 1$, using the observation that the total mass flux involved in faceting must be of the same order of magnitude as the mass flux due to electrotransport. The following calculations of Z^* partly make use of the theory of Mullins for thermal faceting and, consequently, the same pertinent notations have been used.

The continuity of the mass flux across a facet edge at $S_1(-x^*, -y^*)$ or $S_2(x^*, y^*)$ requires

$$\frac{-D_s \nu' \mu_{s1}}{k T [(x^*)^2 + (y^*)^2]^{1/2}} + \frac{D_s}{k T} F_s \quad (1)$$

$$\frac{D_c \nu \Omega \gamma_c}{k T} \left(\frac{\partial^3 y(x, t)}{\partial x^3} \right)_{x^*} + \frac{D_c}{k T} \nu F_c.$$

The variable $y(x, t)$ describes the cross section of the facet and satisfies the differential equation

$$\frac{\partial y(x, t)}{\partial t} = -B \frac{\partial^4 y(x, t)}{\partial x^4} \quad (2)$$

where x^* and y^* are the coordinates at the points where the low index-plane terminates, ν and ν' are the surface mass densities and D_c and D_s are the surface diffusion coefficients on the complex and simple plane, respectively, Ω the atomic volume, γ_c the free surface energy of the complex planes, F_c and F_s the effective forces acting on the migrating surface atoms and $\mu = \mu(\partial^2 y / \partial x^2)$ the chemical potential.

Defining $\nu = \nu'$, $d = D_s / D_c$, $x^* = \omega (B t)^{1/4}$, $k T B = \Omega^2 \nu \gamma D$ and the transformation

$$y(x, t) = \left(\frac{\partial y}{\partial x} \right)_{x^*} (B t)^{1/4} Z \left(\frac{x}{(B t)^{1/4}} \right) \quad (3)$$

the continuity Eq. (1) can be rearranged into Eq. (6):

$$d \left\{ F_s + \left(\frac{\partial^2 y}{\partial x^2} \right)_{x^*} \frac{\gamma_c \Omega}{[(x^*)^2 + (y^*)^2]^{1/2}} \right\} \quad (4)$$

$$= F_c + \gamma_c \Omega \left(\frac{\partial^3 y}{\partial x^3} \right)_{x^*}.$$

With $Z(\omega) = C_3(\omega) Z_3(\omega) + C_4(\omega) Z_4(\omega)$,

according to MULLINS⁸, it follows that

$$dF_s + (x^{*2} + y^{*2})^{-1/2} d \{ C_3 Z_3'' + C_4 Z_4'' \}_{x^*} \quad (5)$$

$$= F_c + (B t)^{-1/2} \{ C_3 Z_3''' + C_4 Z_4''' \}_{x^*}$$

where the differentiation refers to x .

With $x^* (x^{*2} + y^{*2})^{-1/2} = \cos \alpha$ Eq. (5) yields

$$C_3 \{ \omega Z_3''' - d \cos \alpha Z_3'' \} + C_4 \{ \omega Z_4''' - d \cos \alpha Z_4'' \}$$

$$= C_6 \omega, \quad \frac{(B t)^{1/2} (dF_s - F_c)}{m \Omega \gamma_c} = C_6. \quad (6)$$

The right hand side of Eq. (6) will be zero if $D_s F_s = D_c F_c$, i. e., if the average drift velocity is the same on the complex plane as on the simple or low index plane. In this case, Eq. (6) has the form for thermal faceting alone, according to MULLINS⁸. Using Mullins' notation,

$$D_{nm} = \begin{vmatrix} Z_3^{(n)}(\omega) & Z_4^{(n)}(\omega) \\ Z_3^{(m)}(\omega) & Z_4^{(m)}(\omega) \end{vmatrix}$$

and solving for ω the system of three linear equations which results from Eq. (6) and the two other boundary conditions

$$(\partial y / \partial x)_{x^*} = \text{const} = m, \quad n = y^* (x^*, t) / x^* = \text{const},$$

the result is

$$\frac{n}{m} [\omega D_{13}(\omega) - d D_{12}(\omega) \cos \alpha] + D_{03}$$

$$= \frac{d}{\omega} D_{02}(\omega) \cos \alpha + C_6 D_{01}(\omega). \quad (7)$$

Eq. (7) permits the determination of $\omega = x^* / (B t)^{1/4}$ as a function of $d = D_s / D_c$ and F_c and F_s with n and m as geometrical constants.

The relative value of the diffusion coefficients on low index and complex planes permits the determination of the sign of z^* on the surface or vice-versa. This sign is not necessarily identical with that of z^* in the bulk material because of adsorption and the possible variation of the scattering of charge carriers in the surface region. Tracer experiments on surface electrotransport are not yet available.

Two limiting cases will now be discussed: the cases $d = 0$ and $d = \infty$.

a) $d = 0$

Equation (7) takes the form

$$\frac{n}{m} \omega D_{13}(\omega) + D_{03}(\omega) = C_6 D_{01}(\omega), \quad (8)$$

$$\omega = \frac{m}{n} \frac{C_6 D_{01} - D_{03}}{D_{13}}.$$

If ω_0 is the value for faceting without electrotransport, Eq. (8) yields

$$\omega = \omega_0 - \frac{D_{01}(\omega) (B t)^{1/2}}{D_{13}(\omega) n \Omega \gamma_c} F_c \quad (9)$$

where B is proportional to D_c and F_s does not appear anymore since the drift on the low index plane does not contribute. The second term on the right hand side gives the electrotransport correction for surface diffusion-controlled faceting in the limit $D_s/D_c \ll 1$. Since no particular assumption about F has been made, it pertains as well to thermotransport.

b) $d = \infty$

Equation (7) becomes

$$\frac{n}{m} D_{13} \frac{\omega}{d} - \frac{n}{m} D_{12} \cos \alpha + \frac{D_{03}}{d} = \frac{D_{02}}{\omega} \cos \alpha + \frac{D_{01} (B t)^{1/2}}{m \Omega \gamma_c} \left(F_s - \frac{F_c}{d} \right)$$

and in the limit

$$-\frac{n}{m} D_{12} \cos \alpha = \frac{D_{02}}{\omega} \cos \alpha + \frac{D_{01} (B t)^{1/2}}{m \Omega \gamma_c} F_s, \quad (10)$$

$$\omega = -\frac{m}{n} \frac{D_{02} \cos \alpha}{D_{12} \cos \alpha + \frac{D_{01}}{n \Omega \gamma_c} (B t)^{1/2} F_s}.$$

Here B must be proportional to D_s and the drift due to F_c does not contribute. The second term in the denominator represents the transport force correction, which makes $\omega = \omega_0$ if it were zero.

Since there are no published experimental data yet of $x^* = \omega (B t)^{1/4}$, Eqs. (9) and (10) are now used to estimate the effective charge Z^* for the limit $\omega = 0$, using the observation that faceting may be suppressed by electrotransport.

The power series representations of $Z_3(\omega)$ and $Z_4(\omega)$ according to Mullins yield

$$\begin{aligned} Z_3(0) &= -0,78, Z_4(0) = 8,3, D_{01}(0) = -8,3, \\ Z_3'(0) &= 1, Z_4'(0) = 0, D_{02}(0) = +9,57, \\ Z_3''(0) &= -0,58, Z_4''(0) = -6,14, D_{12}(0) = -6,14, \\ Z_3'''(0) &= 0, Z_4'''(0) = 6, D_{13}(0) = +6. \end{aligned}$$

By inserting reasonable values for n , m , Ω , t , γ_c and x^* for tungsten⁹, and taking recent B values from the paper of HO-YI¹⁰ the following results are obtained:

a) $\omega = 0$; $d = 0$

$$F_c(0) = n \frac{D_{13}(0) \Omega \gamma_c}{D_{01}(0) (B t)^{1/4}} x_0^* = e E Z^*$$

(E = electric field, e = electron charge, Z^* = effective charge in units of e).

b) $\omega = 0$; $d = \infty$

$$1 \ll \frac{n}{m D_{02} \cos \alpha} \left(F_s(0) \frac{D_{01}(0) (B t)^{1/2}}{n \Omega \gamma_c} + D_{12} \cos \alpha \right).$$

Table 1.

T [°C]	$ Z^*(0) _{d=0}$	$ Z^*(0) _{d=\infty}$
1600	13,4	< 1,36
1800	3,9	< 0,84
2000	1,9	< 0,36
2200	0,9	< 0,22
2300	0,6	< 0,17

The numerical values indicate very clearly that at temperatures above $(1/2)T_s$ the mass transport due to the superimposed electric field may balance the mass flux of faceting when Z^* values are close to one. The result agrees with rough estimates and shows that Z^* is of an electrostatic nature and the drift by charge carrier scattering can be considered negligible.

As far as the possible sign change of Z^* on surfaces is concerned, the results of KLOTSMAN, TIMOFEEV and TRAKHTENBERG¹¹ deserve special interest. They found that the tracer diffusion of Ag^{110} in silver, copper and gold, and of Sn^{123} in tin is directed towards the cathode, whereas the bulk is transported towards the anode. The authors explain the high absolute values of Z^* with the assumption

⁹ P. ADAM and H. WEVER, Surface Sci. **21**, 307 [1970].

¹⁰ LAI HO-YI, Jernkont. Ann. **151**, 800 [1967].

¹¹ N. K. ARKHIPOVA, S. M. KLOTSMAN, A. N. TIMOFEEV, and I. SH. TRAKHTENBERG, Fiz. Metall. Metalloved. **20**, 159 [1965]; Phys. Met. Metallog. **20** (1), 148 [1965]. — V. N. KAYGORODOV, S. M. KLOTSMAN, A. N. TIMOFEEV, and I. SH. TRAKHTENBERG, Fiz. Metall. Metalloved. **21**, 302 [1966]; Phys. Met. Metallog. **21** (2), 152 [1966]. — S.

M. KLOTSMAN, A. N. TIMOFEEV, and I. SH. TRAKHTENBERG, Fiz. Metall. Metalloved. **14**, 793 [1962]; **16**, 895 [1963]; **16**, 611 [1963]; **23**, 257 [1967]; **24**, 278 [1967]; Phys. Met. Metallog. **14** (5), 140 [1970]; **16** (6), 86 [1963]; **16** (4), 105 [1963]; **23** (2), 63 [1967]; **24** (2), 75 [1967]; Fiz. Tverd. Tela **5**, 3276 [1963]; Sov. Phys. Sol. State **5**, 2396 [1963].

of a cooperative diffusion of several atoms in the stacking fault plane. The sign change can be explained by means of a transition from electron conduction in the bulk to hole conduction in the boundary. The possibility for a change in the conduction mechanism is also indicated by investigations on the electrotransport of In in Ag¹² and Ge in Ge¹³ in the vicinity of dislocations. In principle, the knowledge of diffusion kinetics in the grain boundaries would permit the use of electrotransport experiments as probes for the electronic character of the boundary.

3. Special Effects

It has been established that evaporated thin films become electronic conductors earlier with an electric field across the substrate. The primary islands contact each other at an earlier stage in the field.

This has been investigated, e. g., for silver on glass and gold on mica¹⁴. It cannot be excluded that enhanced surface diffusion on the substrate is involved, but the enhanced coalescence of islands is due mainly to the absence of free charges which can reach the substrate with the vapor beam and can be removed from it by a field crossing the beam¹⁵.

In relation to the electrotransport in thin films is the fact that silver preferably, but also copper and gold, migrate on insulating dielectric substrates used as capacitors in an electric field amounting to several kV/cm. The silver ions migrate even without a field due to an interaction with the surface, but their migration velocity is increased by an external field in the capacitor due to their ionized state¹⁶.

A monograph on the subject of electrotransport and thermotransport on surfaces and interfaces will be published in 1971¹⁷.

¹² V. A. STERKHOV, V. A. PANTELEEV, and P. V. PAVLOV, *Fiz. Tverd. Tela* **9**, 681 [1967]; *Sov. Phys. Sol. State* **9**, 533 [1967].

¹³ V. A. STERKHOV and P. V. PAVLOV, *Fiz. Tverd. Tela* **9**, 643 [1967]; *Sov. Phys. Sol. State* **9**, 495 [1967].

¹⁴ K. L. CHOPRA, *J. Appl. Phys.* **37**, 2249 [1966].

¹⁵ R. A. ZHILINSKAS, L. A. YAKUCHENIS, and P. K. TAMUTIS, *Sov. Phys. Sol. State* **11**, 410 [1969].

¹⁶ S. W. CHAIKIN, J. JANNEY, F. M. CHURCH, and CH. W. MCCLELLAND, *Indust. and Eng. Chem.* **51**, 299 [1959].

¹⁷ H. WEVER, G. FROHBERG, and P. ADAM, *Elektro- und Thermotransport in Metallen*, accepted for publication by J. A. Barth, Leipzig 1971.