

Potential and current distributions along resistive electrodes

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A simple theory of current and potential distributions along resistive electrodes is re-examined and generalized for non-linearized Tafel behavior. A model of a passivating electrode is discussed and the generalized theory extended to derive expressions for the current and potential profiles along a partially passivated electrode. The relevant expressions permit a predictive analysis of the feasibility of using the electrochemical passivation method for etch-stop control in fabrication of thin, single crystal silicon structures produced by anisotropic deep etching.

1. Introduction

Current and potential distributions in electrochemical cells have been of interest in a number of applications including electrolytic machining, batteries under high power drains, high temperature batteries or gas diffusion electrodes. Recently, the problem of potential distribution along resistive semiconductor electrodes arose in connection with the fabrication of miniature sensor devices [1]. These devices often embody thin single crystal silicon structures produced by anisotropic 'deep' etching. The etch stop can be affected by a number of methods of which electrochemical passivation at the desired depth seems particularly suitable when electronic devices must be incorporated into the remaining semiconductor wafer. The feasibility of this type of etch-depth control depends on the size of the electronic components and on the silicon properties. An analysis which would predict the electrochemical response of the semiconductor to the etching conditions and define the final geometry requires a knowledge of the potential and current distribution along the resistive semiconductor electrode. For this purpose we have re-examined and generalized the simple linear theory for non-passivating electrodes [2] and extended it to the passivating case.

2. Non-passivating electrode

2.1. The model

Consider a flat electrode of specific resistivity ρ , length L , width w and thickness t (cf. Fig. 1). The electrode is fully immersed in an electrolyte, polarized against a counterelectrode of infinite conductivity and potentiostated at an applied potential, V_L at the point $y = L$.

Due to the ohmic drop in the electrode, the potential decreases from the applied value, V_L , to V_0 at the tip of the electrode; the potential increment at a point y is given by

$$V'_y \equiv (\delta V / \delta y)_y = I_y \rho / wt \quad (1)$$

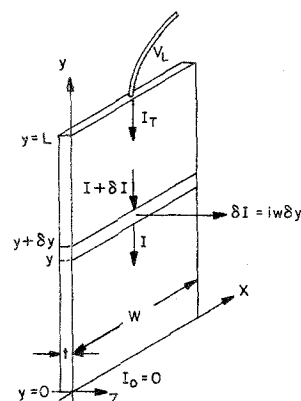


Fig. 1. Schematic diagram of the model electrode.

where I_y is the current collected between points $y = 0$ and $y = y$.

It is assumed that: (1) no ohmic drop exists between the reference and test electrodes; (2) current density, i_y , is uniform along the z axis. The current density which represents the current increment in the electrode length δy can be written as:

$$i_y = I'_y / w. \quad (2)$$

2.2. Exponential rate equation

It is assumed that the rate of the electrode reaction obeys the Tafel equation:

$$i_y = i_0 \exp(bV_y), \quad (3)$$

where i_y is the current density at a point y , determined by the local overpotential, V_y ; i_0 is the exchange current density; $b \equiv \alpha F / RT$; α is the transfer coefficient. Both current density and overpotential are taken as positive in all cases.

2.2.1. Current and current density profiles. From Equations 2 and 3

$$I'_y = wi_0 \exp(bV_y) \quad (3a)$$

The current distribution can be found by differentiation

of Equation 3a to yield:

$$I'' = I' b V' \quad (4)$$

From Equations 1 and 4

$$I'' = A I I' \quad (5)$$

where

$$A \equiv b \rho / w t \quad (6)$$

Integration of Equation 5 yields*

$$I' = A I^2 / 2 + C_1 \quad (7)$$

Using the boundary conditions $I_L = I_T$ (where I_T is the measured total current) or $I_0 = 0$, the integration constant in Equation (6) becomes, respectively

$$C_1 = I_L' - A I_L^2 / 2 \equiv w i_0 \exp(b V_L) - A I_L^2 / 2 \quad (8)$$

or

$$C_1 = I_0' \equiv w i_0 \exp(b V_0) \quad (9)$$

For the given electrode and electrode reaction the value of C_1 depends only on the applied potential. It can be obtained for each V_L from the measured value of I_T and from a polarization curve determined in a separate experiment carried out in the same electrolyte at a thin layer of the same electrode material backed by a conductive metal. The latter measurement supplies not only values of I_L' , but also that of the Tafel slope, $1/b$, necessary for calculation of A . Equations 8 and 9 give V_0 as a function of the measurable quantities: applied potential V_L and total current, I_T .

The integrated form of Equation 7 depends on the sign of C_1 . It follows from Equation 9 that $C_1 > 0$ since, by definition, $I' \equiv \delta I / \delta y > 0$. Upon integration Equation 7 yields:

$$\sqrt{2/AC_1} \arctan(I\sqrt{A/2C_1}) = y + C_2 \quad (10)$$

Using the boundary condition $I_0 = 0$ in Equation 10 yields $C_2 = 0$. Thus, Equation 10 can be rewritten as:

$$I_y = (\sqrt{2C_1/A}) \tan(y\sqrt{AC_1/2}) \quad (11)$$

Also,

$$I_T = (\sqrt{2C_1/A}) \tan(L\sqrt{AC_1/2}) \quad (12)$$

For reduced variables $\bar{I}_y \equiv I_y/I_T$ and $\bar{y} \equiv y/L$,

$$\bar{I}_y = \tan(\bar{y}F) / \tan F \quad (13)$$

where $F \equiv \sqrt{L^2 AC_1/2}$.

The values of C_1 and I_T vary with the applied potential; however, both can be determined from measurement (see above) to yield the current distribution, \bar{I}_y .

* The differential Equation 5 is solved by defining $I' \equiv n$, differentiating n with respect to I and expressing it as follows:

$$\delta n / \delta I \equiv \{ \delta(\delta I / \delta y) / \delta y \} \cdot (\delta y / \delta I) = I' / n,$$

from which

$$A n I = n \delta n / \delta I \quad (5a)$$

Dividing by n (which is by definition always > 0) and integrating Equation 5a results in

$$n \equiv I' = A I^2 + C_1$$

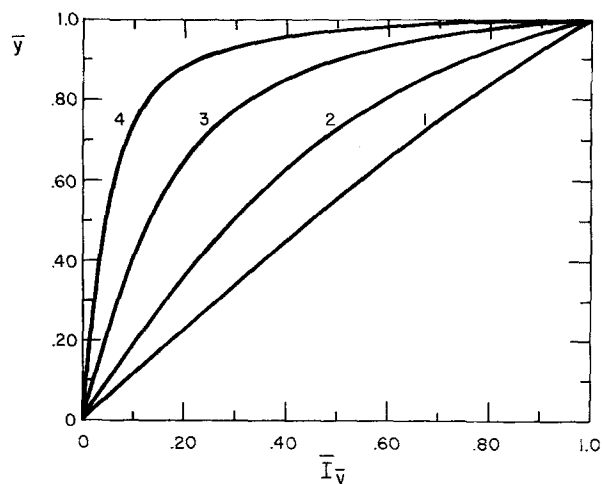


Fig. 2. Current profiles along a resistive electrode for $A = 10^5 \text{ A cm}^{-1}$, $i_0 = 10^{-6} \text{ A cm}^{-2}$ and $b = 20 \text{ V}^{-1}$: 1, $V_L = 0.5 \text{ V}$; 2, $V_L = 0.375 \text{ V}$; 3, $V_L = 0.250 \text{ V}$; 4, $V_L = 0.125 \text{ V}$.

They can also be numerically calculated *a priori** from the polarization curve using Equations 8 and 12.

A family of current profiles, \bar{I}_y , calculated for the reduced variable, \bar{y} , is shown in Fig. 2. For values of $\sqrt{L^2 AC_1/2}$ ($\equiv F$) lower than ~ 0.5 (i.e. when $\tan(F) \approx F$), the current profile (Equation 13) is nearly linear with tolerance better than 10%. As F increases from 0.5 to $\pi/2^\dagger$, the current profile departs from linearity in the fashion exemplified by curves in Fig. 2. In these examples the increase of F was effected by increasing the values of the applied potential, V_L , while the product of geometric parameters, resistivity and Tafel slope, as well as the exchange current density were kept constant.

The current density distribution, obtainable from Equation 2 and the differential of Equation 11, is given by:

$$i_y = C_1 / w \cos^2(yF) \quad (14)$$

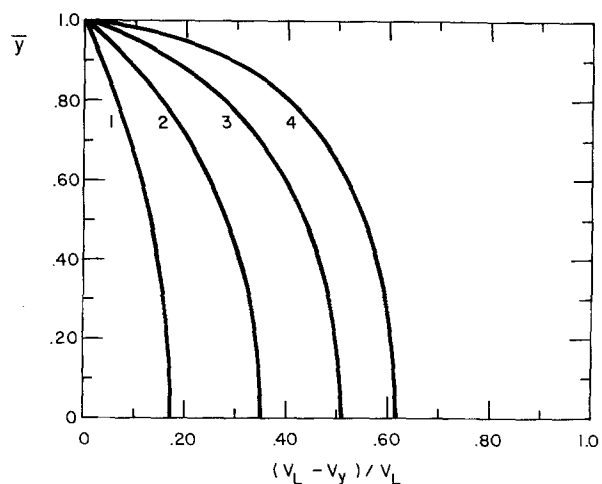


Fig. 3. Potential profiles along a resistive electrode for numerical values as in Fig. 2.

* Programs for computations necessary to obtain numerical solutions to all expressions in this paper are available at request from the authors.

† The necessity of limiting computations to the region bounded by 0 and $\pi/2$ arises from the use of the Tafel Equation 3 rather than the Butler-Volmer-type expression, which would permit the currents and overpotentials to become negative.

2.2.2. *Potential profile.* From Equations 1 and 11:

$$\int_{y_p}^{L} \delta V = (\rho/wt)\sqrt{2C_1/A} \int_{y_p}^L \tan(\bar{y}F)\delta\bar{y} \quad (15)$$

from which, upon integration

$$V_L - V_y = 2/b \ln(\cos(\bar{y}F)/\cos F) \quad (16)$$

The potential drop over the entire electrode length is given by:

$$V_L - V_0 = -(2/b) \ln \cos(F). \quad (17)$$

A family of numerically computed potential profiles along resistive electrodes is shown in Fig. 3 for F values corresponding to those used to compute Fig. 2.

2.3. Linear approximation

Under low overpotential conditions, when the Tafel equation can be linearized, I' is given by:

$$I' \equiv iw = i_0w(1 + bV) \quad (18)$$

Differentiation of Equation 18 yields:

$$I'' = \{i_0wb\}\delta V/\delta y \quad (19)$$

From Equations 1 and 19

$$I'' = k^2I \quad (20)$$

where

$$k^2 \equiv i_0b\rho/t \quad (20a)$$

Upon integration Equation 20 yields

$$I_y = D_1 \exp(ky) + D_2 \exp(-ky) \quad (21)$$

Using boundary conditions $I_0 = 0$ and $I_L = I_T$ the current profile is found as

$$I_y = I_T \sinh(ky)/\sinh(kL), \quad (22)$$

the current density profile is given by

$$i_y = I_T k \cosh(ky)/w \sinh(kL) \quad (23)$$

and the potential profile obtained by integration of Equation 1 using Equation 22 becomes:

$$V_L - V_y = \frac{I_T \rho [\cosh(kL) - \cosh(ky)]}{kwt[\sinh(kL)]} \quad (24)$$

All calculations in this section, as well as in Section 3.2, were made in terms of actual variables, since rewriting them in reduced form is trivial and unnecessary.

3. Passivating electrodes

When the value of the applied potential, V_L , exceeds that of the passivating potential, V_p , a part of the electrode will passivate. In order to calculate the length of the passivated part as a function of the applied overpotential, consider a model which differs from that described in Fig. 1, in that the upper part of the electrode between $y = L$ and y_p is passivated (cf. Fig. 4).

Equations derived in Section 2.2 apply in the region $y = 0$ to y_p , with suitably changed boundary con-

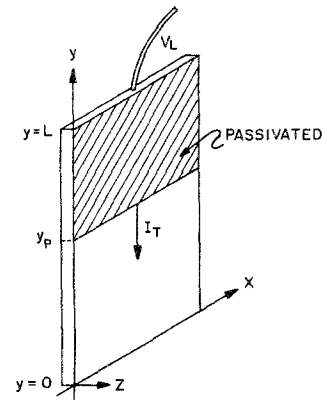


Fig. 4. Schematic diagram of a partially passivated model electrode.

ditions, i.e.:

$$I'_p = wi_p, \quad (25)$$

and

$$I_p = I_T, \quad (26)$$

where i_p is the passivating current density. The passivating current density and passivation potential V_p are found from the polarization curve obtained in a separate experiment (cf. Section 2.2.1).

The potential drop within the passivated part of the electrode is given by

$$V_L - V_p = I_T(L - y_p)\rho/wt. \quad (27)$$

3.1. Exponential rate equation

Expression 12, previously derived for the total current, contains a constant C_1 defined by Equation 8. For the present case, C_1 must be replaced by

$$C = wi_0 \exp(bV_p) - AI_T^2/2. \quad (8a)$$

Rewriting Equation 12 in the form

$$I_T = (\sqrt{2C/A}) \tan(\bar{y}_p F), \quad (12a)$$

and inserting Equation 12a into Equation 27 one obtains

$$V_L - V_p = (\sqrt{2C/A}) \tan(\bar{y}_p F)(1 - \bar{y}_p)R \quad (28)$$

where R is the electrode resistance given by $\rho L/wt$.

The transcendental Equation 28 defines the reduced value of the electrode length $(1 - \bar{y}_p)$, which becomes passivated by the applied potential V_L . The equation can be easily solved numerically*.

Note that Equation 28 has a maximum, since at $\bar{y}_p = 1$ and at $\bar{y}_p = 0$ the left hand side of Equation 28 becomes 0, while the intermediate values between these points are finite and positive. A few potential profiles calculated for various values of the electrode resistance (other parameters being kept constant) are shown in Fig. 5. With decreasing electrode resistance, the maxima increase until they reach the value of $y_{p,max} \approx 0.5$ under limiting conditions described in Section 3.2.

* The simplest method of solution and the corresponding program are available from the authors.

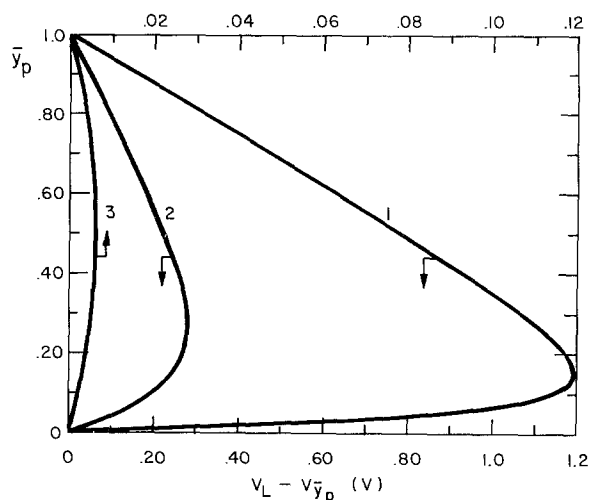


Fig. 5. Graphical representation of Equation 28 for $b = 20 \text{ V}^{-1}$, $i_0 = 10^{-6} \text{ A cm}^{-2}$, $i_p = 5 \times 10^{-3} \text{ A cm}^{-2}$; curves 1 and 2, lower abscissa; curve 3, upper abscissa: 1, $A = 10^5 \text{ A cm}^{-1}$ ($R = 5000 \Omega$); 2, $A = 10^4 \text{ A cm}^{-1}$ ($R = 500 \Omega$); 3, $A = 100 \text{ A cm}^{-1}$ ($R = 5 \Omega$).

The physical origin of the maxima on potential profiles exemplified in Fig. 5 can be understood, as follows. Starting with an unpassivated electrode and applying a potential higher than the passivating value will result in a portion of the electrode near $\bar{y} = 1$ ($y = L$) becoming passivated. With the increase of V_L the length of the passivated portion will increase until the applied potential reaches the value $V_{L,\text{max}}$ which passivates the length $(1 - \bar{y}_{p,\text{max}})$. Any further increment, δV , of the applied potential will cause an additional increment of passive layer length which will result in a reduced ohmic drop ($V_L - V_p$) in the passivated part. This, in turn, will cause the potential at the boundary between passivating and non-passivating portions to exceed the value of V_p . The argument can be applied to any point below $\bar{y}_{p,\text{max}}$ down to $\bar{y} = 0$. Thus, any increment of applied potential above $V_{L,\text{max}}$ will result in the passivation of the entire electrode. The parts of lines in Fig. 5 below maxima have no physical counterpart, since, ideally, an infinitesimally small increment of applied potential, V_L , above the $V_{L,\text{max}}$ value results in total insulation of the entire electrode by the passivating layer. The value of the applied potential sufficient for the passivation of the entire electrode can be (most conveniently) obtained numerically from Equation 28.

3.2. Linear approximation

Under low overpotential conditions the current profile

within the region bounded by $y = 0$ and y_p is given for non-passivating electrodes by Equation 22. This, rewritten for the passivating electrode model (cf. Fig. 4) becomes:

$$I_y = I_T \sinh(ky)/\sinh(ky_p) \quad (22a)$$

Differentiation of Equation 22a yields:

$$I'_y = I_T k \cosh(ky)/\sinh(ky_p) \quad (29)$$

At $y = y_p$, $I'_p = wi_p$, $I_p = I_T$, and thus

$$I_T = [wi_p \tanh(ky_p)]/k \quad (30)$$

The potential drop along the passivated part of the electrode, $(L - y_p)$ is given by Equation 27. From Equations 27 and 30:

$$V_L - V_p = (i_p q/kt)(L - y_p)[\tanh(ky_p)] \quad (31)$$

Equation 31 defines y_p in terms of known parameters, with k values given by Equation 20a.

Again, the function has a maximum as y_p decreases from L to 0. The value of y_p for this maximum can be found by equating the first derivative of Equation 31 to zero, which yields

$$k(L - y_{p,\text{max}}) = 0.5 \sinh(2ky_{p,\text{max}}) \quad (32)$$

For $ky_p < 0.5$, $\sinh(2ky_p) \approx 2ky_p$ and

$$y_{p,\text{max}} \approx 0.5L \quad (33)$$

i.e. under these conditions, the function has a maximum close to $L/2$ and any potential increment over the value of V_L which passivates the half-length is sufficient to passivate the entire electrode.

Also, for $ky_p < 0.5$, $\tanh(ky_p) \approx ky_p$ and Equation 31 can be rewritten as

$$V_{L,\text{max}} - V_p = (i_p q/t)(L^2/4) \quad (34)$$

The experimental verification of the validity of this simplified model of current and potential distribution along a resistive passivating electrode has been described in a separate publication [1]. Expressions presently derived can be used to define conditions which allow electrochemical passivation to effect etch-stop control during anisotropic deep etching of silicon, as shown in Ref. [1].

References

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- [2] B. E. Conway and E. Gileadi, *Can. J. Chem.* **41** (1963) 2447.