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K. Uosaki and H. Kita

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COMMENTS

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Each issue of the **Journal** will have a section of "Comments." In this section, we provide a means via short pieces, *i.e.*, one column or less, to applaud, dispute, or otherwise discuss the papers published in the **Journal.** Space will be provided for one response by the paper's author(s) to each comment.

Since space available in each issue for the "Comments" section is limited, it is important to be concise.

Comments should be sent to the Editor, Dr. Norman Hackerman, President's Office, Rice University, P.O. Box 1892, Houston, TX 77251.

This is the first appearance of the "Comments" section.

Norman Hackerman
Editor

Effects of the Helmholtz Layer Capacitance on the Potential Distribution at Semiconductor/Electrolyte Interface and the Linearity of the Mott-Schottky Plot

K. Uosaki and H. Kita
pp. 895-897, Vol. 130, No. 4

H. Gerischer:[1] The paper of the above authors contains some serious errors in the equations quoted. The last term in the numerator of Eq. [4] must read $n_0 \cdot e^{ys}$, not n_0. Equations [8] and [9] represent the approximation for the case of a depletion layer in an n-type semiconductor and should read correctly

$$Q_{sc} = \left(2e\epsilon\epsilon_0 N_D\right)^{1/2}\left(\Delta\psi_{sc} - \frac{kT}{e}\right)^{1/2} \qquad [8]$$

$$C_{sc} = \left(\frac{e\epsilon\epsilon_0 N_D}{2}\right)^{1/2}\left(\Delta\psi_{sc} - \frac{kT}{e}\right)^{-1/2} \qquad [9]$$

Besides this, the paper gives a misleading impression of the relation between the space-charge layer capacitance and the Helmholtz double-layer capacitance of normal semiconductor electrodes since the calculations are made with an unusually high carrier concentration in the bulk ($n_0 = N_D = 10^{19}$ cm^{-3}) and an exceptionally large dielectric constant ($\epsilon = 173$). Most semiconductors such as ZnO, CdS, CdSe, GaP, GaAs, Si, MoS_2, $MoSe_2$, WS_2, and WSe_2, have static dielectric constants in the order of 6-12. Usual carrier concentrations are in the order of 10^{16}–10^{18}. With such values, the space-charge capacity is by far smaller than for the example given in this paper. Consequently, the relation between the variation of the voltage drop in the Helmholtz double layer and the voltage applied to the whole interface (referred to the flatband potential) is drastically reduced in comparison to the data given in Fig. 1 of this paper.

More realistic data are shown in Fig. 1a and b, which was derived for depletion layers in the absence of surface states from the following relations, being valid for $y_{sc} > 4$

$$Q_{sc} = (2\epsilon\epsilon_0 kTN_D)^{1/2}\,(y_{sc} - 1)^{1/2} \qquad [1]$$

$$C_{sc} = e\left(\frac{\epsilon\epsilon_0 N_D}{2kT}\right)^{1/2}\left(y_{sc} - 1\right)^{-1/2} \qquad [2]$$

$$y_{sc} = \frac{e\Delta\psi_{sc}}{kT} \text{ with } \Delta\psi_{sc} = \psi_b - \psi_s \qquad [3]$$

$$y_H = \frac{e\Delta\psi_H}{kT} = 2\,\frac{C_{sc}}{C_H}\left(y_{sc} - 1\right) \qquad [4]$$

The voltage drop in the space-charge layer $\Delta\psi_{sc}$ and in the Helmholtz layer $\Delta\psi_H$ is represented in Eq. [3] and [4] in terms of kT/e units (25 mV at T = 298 K). With $\epsilon_0 = 8.854 \cdot 10^{-14}$ As/V · cm and $C_H = 10$ μF, the relation $[y_H/(y_H + y_{sc})]$ has been calculated and is plotted against $y_H + y_{sc}$ in Fig. 1a for $N_D = 10^{19}$ and 10^{17} with $\epsilon = 173$, and in Fig. 1b for the same donor concentrations with $\epsilon = 10$. One sees that the relative contribution of y_H to the whole potential drop $y_H + y_{sc}$ is very small for $N_D = 10^{17}$ and $\epsilon = 10$, representing the usual situation in semiconductor electrochemistry.

The necessary correction for the variation of $\Delta\psi_H$ in the extrapolation to the flatband potential in a Mott-Schottky plot has been correctly derived in the paper of DeGryse *et al.*[2] and quoted as Eq. [10] in the above paper. It is, however, also drastically reduced, if the dielectric constant has a normal value and the donor density is

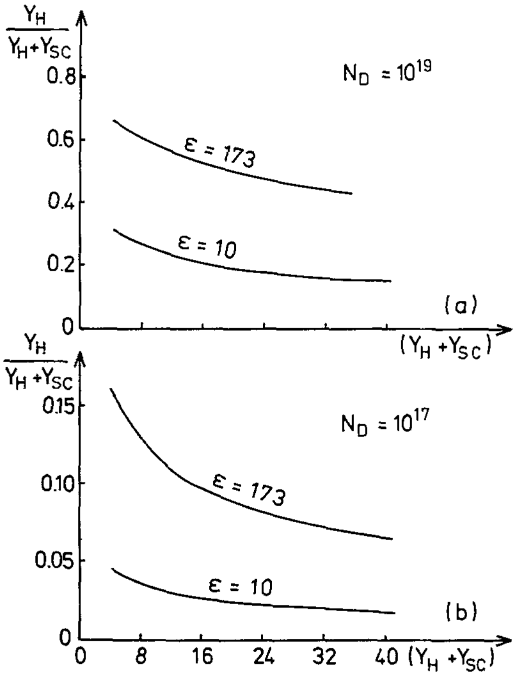

Fig. 1. Relative contribution of the voltage drop variation in the Helmholtz double layer, y_H, to the whole voltage variation over the semiconductor/electrolyte interface, $y_H + y_{sc}$, for two different donor concentrations and two different dielectric constants of the semiconductor. Helmholtz double-layer capacity: 10 μF.

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[2] R. De Gryse, W. P. Gomes, F. Cordon, and J. Vennik, *This Journal*, 123, 711 (1975).

smaller than 10^{19}. DeGryse *et al.* have found with $C_H = 10$ μF as correction for the extrapolated value of V_{FB} at an n-type semiconductor with $\epsilon = 173$ and $N_D = 10^{19}$ the large value of −0.12V. From the correction formula, $\Delta V_H = -[\epsilon\epsilon_0 e N_0/2C_H^2]$, one obtains with $\epsilon = 10$, instead of 173, only −7 mV, and with $N_D = 10^{17}$ instead of 10^{19}, this correction is fully negligible.

It is certainly important to be aware of the possibility that the potential drop in the Helmholtz double layer can vary with the applied voltage. However, one should also see that the importance of this effect depends very critically on the doping level and the magnitude of the dielectric constant. A variation in $\Delta\psi_H$ will much more often be due to the presence of surface states with a density in the order of 10^{13} cm^{-2} within a narrow range of energies.

K. Uosaki and H. Kita:[3] We must admit that Eq. [4], [8], and [9] of our paper contain misprints, as Professor Gerischer has pointed out. But note all the calculations have been carried out by using proper equations.

Although Gerischer commented that our calculations were made only with an unusually high carrier concentration in the bulk ($n_0 = N_D = 10^{19}$ cm^{-3}), we calculated the potential distribution with a wide range of carrier concentrations (10^{16} cm^{-3} ~ 10^{20} cm^{-3}) as shown in Fig. 1 of our paper.

Gersicher said this paper gives a misleading impression of the relation between the space-charge layer capacitance and the Helmholtz double-layer capacitance of normal semiconductors. However, we think it is important to stress the effects of the Helmholtz double-layer capacitance on the potential distribution and linearity of the Mott-Schottky plot because many semiconductor electrochemists simply ignore the Helmholtz layer capacitance without considering its physical significance.

As far as the effect of the Helmholtz layer capacitance on the linearity of the Mott-Schottky plot is concerned, we supported the general conclusion of De Gryse *et al.*[4] but pointed out that the real Mott-Schottky plot deviates from the linear line calculated by using Eq. [10] of our paper, which was derived by De Gryse *et al.* with the Mott-Schottky approximation,[4] near the flatband potential.

Galvanostaircase Polarization

S. T. Hirozawa

pp. 1718-1721, Vol. 130, No. 8

F. Mansfeld:[5] Hirozawa's paper gives an interesting application of a very simple experimental technique. However, some discussion of the conclusions by the author concerning pitting of aluminum is necessary to avoid even more confusion in the general topic of "critical potentials" than there exists now. There is no theoretical justification in the paper for the claim that extrapolation of the E-I curves to $I = 0$ leads to the breakdown potential E_b for increasing I and to the protection potential E_{prot} for decreasing I. The statement "E appears to have no direct relevance to localized corrosion; however, it seems to have indirect relevance" is quite puzzling in the light of the previous claim concerning E_b and E_{prot}.

In analyzing Hirozawa's experiment, one could conclude that the application of the first constant-current step produces pitting. The corresponding potential maximum is probably the pitting potential. While the current is increased stepwise, the kinetics in the growing pits are measured, since there is not much contribution from the passive surface. The observed small hysteresis in uninhibited solutions is due to changes in the pit growth kinetics, pit size, conductivity in the pits, etc. In the inhibited solutions, the electrochemical kinetics in the growing pit are altered, owing to the presence of the inhibitor. As the pits grow (which they do even when the current is decreased), hysteresis occurs because the inhibitor concentration in the pit decreases and for other, presently unknown reasons. As can be seen from Hirozawa's data (his Fig. 3 and 4), the electrochemical kinetics in this case tend to return to those for the uninhibited case.

In summary, the galvanostaircase method applied to Al shows some promise for the study of electrode kinetics in growing pits. However, the claim that the breakdown and protection potentials can be determined from Hirozawa's data cannot be accepted unless it is substantiated by further theoretical and experimental work.

S. T. Hirozawa:[6] Mansfeld claims that extrapolation for E_b and E_{prot} from GSCP curves has not been theoretically justified and would only increase the confusion presently existing concerning the critical potentials. Others (7-9) using galvanokinetic or galvanostatic polarization techniques have used terms that are analogous to E_b and E_{prot} (paragraph 1 of my paper).

It is true that we have no theoretical justification for the use of the E_b and E_{prot}, but we do have experimental justification using long term constant potential corrosion tests (second paragraph of my paper). The two main causes for the confusion concerning the critical potentials are nomenclature and the use of potential-controlled polarization techniques under highly passivating conditions which lead to induction time effects and current hysteresis.

For Al under highly passivating conditions, *e.g.*, in antifreeze coolants, E_b (which is often considered to be the pitting potential) appears to have no direct relevance to localized corrosion because E does not have to be raised above E_b, to initiate pitting: one only needs to raise E above E_{prot} to initiate pitting. Hence, E_b is not a critical potential, but it does have indirect relevance because the greater the difference between E_{prot} and E_b, the greater is the tendency for crevice corrosion.

Mansfeld's statement that "in analyzing Hirozawa's experiment, one could conclude that the application of the first current step produces pitting" is true for Fig. 3 and 4, where the evidence for pitting is quite apparent. Pitting occurs on metals that are passivated, preferably by a layer of insoluble salts. In Fig. 1 and 2, pitting is not evident. Chloride is nonpassivating; therefore, the corrosion is general and not localized. The passivation of Al by nitrate is unique. The first current step does not break down the passive layer, but rather it builds it up further. Hence, the use of the term, E_b, is not appropriate; it is used here for the want of a better name. The gradual change of potential during the first two steps probably indicates changes in the resistance of the inner oxide layer as well as the distribution of nitrate within the passive layer under the influence of the electric field.

In conclusion, the GSCP method should dispel some of the confusion related to the critical potentials, induction effects, and the scan rate, hysteresis, and charge effects on the value of E_{prot}.

The Effect of Stress on the Redistribution of Implanted Impurities in GaAs

J. Kasahara, Y. Kato, M. Arai, and N. Watanabe

pp. 2275-2279, Vol. 130, No. 11

C. Blaauw:[10] The authors analyze the effect of stress, induced by a plasma silicon nitride capping film, on the diffusion constants for Si and Se implants in GaAs. Several incorrect assumptions are made, which affect analysis of the results. For example, Eq. [1] implies that the intrinsic stress of the capping film is taken to be zero, whereas it is well known that plasma silicon nitride films

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[3] Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060, Japan.

[4] R. De Gryse, W. P. Gomes, F. Cardon, and J. Vennik, *This Journal*, **123**, 711 (1975).

[5] Rockwell International Science Center, Thousand Oaks, California 91360.

[6] BASF Wyandotte Corporation, Wyandotte, Michigan 48192.

[7] S. Smialowska and M. Czachor in "Localized Corrosion," R. W. Staehle, B. F. Brown, J. Kruger and A. Agrawal, Editors, p. 353, NACE-3, Houston (1974)

[8] A. Broli, H. Holtan, and K. L. Prestud, *Corrosion*, **30**, 427 (1974).

[9] K. Nisancioglu and H. Holtan, *Corros. Sci.*, **18**, 835 (1978).

[10] Bell-Northern Research, Ottawa, Ontario, Canada K1Y 4H7.

are deposited in a state of tensile stress (11, 12). More seriously, the analysis of the diffusion coefficients in terms of jump frequency and vacancy concentration rests on the assumption that the substrate-induced stress at 850°C is proportional to the thickness of the capping film. This assumption is not justified, as the properties of plasma silicon nitride are not necessarily uniform throughout the film. We have carried out stress measurements as a function of film thickness, for plasma silicon nitride on GaAs, which show that both the intrinsic stress and the temperature dependence of the stress depend on film thickness (2). Extrapolating stress *vs.* temperature curves to 850°C, we find that the substrate-induced stress for a 0.4 μm film is only approximately 40% larger than that of a 0.1 μm film deposited under the same conditions. If a similar relationship were to apply for the work under discussion, this would move the data points at ≈0.3 μm in Fig. 7, of the paper in question well to the left on the corresponding stress scale, in good agreement with the linear solid line of this figure. This would imply that there is no need to assume a stress-dependent vacancy concentration within the region of investigation.

J. Kasahara:[13] I appreciate the interest and useful reading of our paper.

Basically, I agree with the comments, which pertain mainly to our Fig. 7. Although further quantitative study is necessary, if the intrinsic stress and thickness-dependent temperature dependence of the stress have some influence, the scale of the lower axis for the stress might be modified. Dr. Blaauw discussed this subject in his Ref. (2), which was not available when our manuscript was being prepared. Also, it is difficult to apply his data directly to our data, because the deposition system for SiN is different. Further, considering the behavior of the stress dependence of the diffusion of Zn, know to be by an interstitial-substitutional mechanism, and the result of Se with about 0.6 μm of thicker SiN, I think it is too important to ignore the effect of the vacancy concentration. Further discussion probably requires measuring the stress *in situ* at the annealing temperature investigated.

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[11] A. K. Sinha, H. J. Levinstein, and T. E. Smith, *J. Appl. Phys.*, **49**, 2423 (1978).

[12] C. Blaauw, *J. Appl. Phys.*, **54**, 5064 (1983).

[13] Sony Corporation Research Center, Yokohama 240, Japan.