EFFECT OF STATISTICAL FERMI LEVEL SHIFT ON THE MEYER–NELDEL RULE OF a-Si: H CONDUCTIVITY

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Effect of the statistical Fermi level shift on the Meyer–Neldel rule of a-Si: H conductivity was studied using the temperature dependence of MOSFET conductivity. A model is presented in which the temperature dependence of surface band bending in a MOSFET should compensate for the statistical Fermi level shift of bulk a-Si: H. This compensation is verified by the SiO₂ thickness dependence of the MOSFET conductivity. The pre-exponential factor obtained by analysis of the temperature dependence of MOSFET conductivity does not show the Meyer–Neldel rule. It is therefore concluded that the Meyer–Neldel rule observed in bulk a-Si: H conductivity is predominantly caused by the statistical Fermi level shift.

1. Introduction

The temperature dependence of dark conductivity of a-Si: H is well known to obey the Meyer–Neldel empirical rule [1,2]. This rule involves two problems which need to be solved. The first is why the pre-exponential factor \( \sigma_0 \) of the conductivity varies with the activation energy \( E_a \). The second is why \( \sigma_0 \) is much greater than the product \( N_c e \mu_0 \), where \( N_c \), \( e \) and \( \mu_0 \) are effective conduction band level density, electron charge and electron microscopic mobility respectively. As discussed by many authors, the origin of this rule has been attributed to such possibilities as the mobility edge shift with temperature [3], surface band bending [4], electron phonon interaction [5] and statistical Fermi level shift [6].

In particular, however, the model of mobility edge shift with the temperature cannot explain the doping effect on \( \sigma_0 \) as discussed by Fritzsche [2]. On the other hand, the surface band bending model cannot explain large \( \sigma_0 \). This limitation arises from the assumption that the current in the coplanar type sample flows predominantly in a surface space charge layer. It should be noted that the intrinsic \( \sigma_0 \) of the surface space charge layer must be further greater than \( \sigma_0 \) obtained by assuming that current flows uniformly in the bulk. This is because the space charge layer is much thinner than bulk a-Si: H. It therefore becomes more difficult to explain the large \( \sigma_0 \). Although Solomon [7] has suggested the temperature dependence of the surface band bending in order to

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explain the large $\sigma_0$, it is not clear what physical process causes this effect. Moreover, the sign of the temperature dependence of the surface band bending which he assumed is opposite to that which we will demonstrate in this paper.

The statistical Fermi level shift with the temperature, which is commonly observed in crystalline semiconductors, strongly affects the temperature dependence of the conductivity. It is important to estimate the significance of this effect in the Meyer–Neldel rule. However, it is difficult to estimate the statistical Fermi level shift in each doping level sample, because the degree of the statistical shift depends on the detail charge distribution in the localized states near the Fermi level position.

Thus, it is preferable to develop an experimental method in which the effect of the unknown statistical Fermi level shift on the conductivity temperature dependence can be neglected. The $\sigma_0$ obtained by this method should be compared with the already reported one which is obtained from an ordinary coplanar geometry sample. Several trials combining the temperature dependences of conductivity and thermopower [6] were performed for this purpose. It is difficult to directly obtain $\sigma_0$ which is not affected by the statistical shift, however, because the thermopower contains the heat transport term.

We found that the temperature dependence of the conductivity of MOSFET having a thick oxide film is not affected by the statistical shift at the bulk a-Si:H. This is because the effect of the statistical shift is automatically compensated by the temperature dependence of the surface band bending. This model is verified by the phenomenon in which the temperature dependence of the conductivity at the a-Si:H and SiO$_2$ interface of the MOSFET depends on the SiO$_2$ thickness.

The conductivity of the MOSFET is, of course, affected by the surface band bending. It can be analysed by solving the Poisson equation and can then be compared with the conductivity obtained from the ordinary coplanar type sample. As a result, it is clarified that $\sigma_0$ obtained by the analysis of the MOSFET conductivity, which is not affected by the Fermi level statistical shift, does not show the Meyer–Neldel rule and is comparable with the product $N_v e\mu_0$. It is therefore concluded that the Meyer–Neldel rule observed in the coplanar geometry sample is caused by the Fermi level statistical shift.

2. Temperature dependence of MOSFET conductivity

The mechanism in which the Fermi level statistical shift is compensated by the temperature dependence of the surface band bending in a MOSFET is demonstrated in this section. The band bending profile and an equivalent circuit of MOS are outlined in fig. 1, where $C_i$ and $C_D$ are the capacitances of the insulator and the space charge layer of a-Si:H respectively.

The applied gate voltage is divided by the two capacitors and the division ratio is determined by their capacitances. If the Fermi level statistically shifts
with the temperature, the $C_D$ varies with temperature. This means that the ratio of the gate voltage divided by the two capacitors changes with the temperature. The surface band bending $\psi_s$ of a-Si:H at the interface of a MOSFET is represented by the voltage applied to the $C_D$. Therefore, $\psi_s$ varies with the Fermi level statistical shift.

Let $Q_s$ be the charge at the surface of a-Si:H induced by the electric field. The voltage applied on SiO$_2$ is expressed by Gaussian law as $d_i Q_s / \varepsilon_i$, where $d_i$ and $\varepsilon_i$ are the thickness and dielectric constant of SiO$_2$ respectively. The applied gate voltage $V_g$ is

$$V_g = V_F + \psi_s / e + d_i Q_s / \varepsilon_i,$$  \hspace{1cm} (1)

where $V_F$ is the flat band voltage and $\psi_s$ is the band bending at the interface of a-Si:H and SiO$_2$. If the Fermi level statistically shifts with the temperature under a constant gate voltage, a variation of $Q_s$, i.e. $\psi_s$, occurs. For the sake of simplicity, we neglect the temperature dependence of $V_F$. Then, from eq. (1),

$$\frac{\partial \psi_s}{\partial T} = - \frac{d_i e}{\varepsilon_i} \frac{\partial Q_s}{\partial T} = \frac{d_i e}{\varepsilon_i} \left( \frac{\partial Q_s}{\partial E_F} \frac{\partial E_F}{\partial T} + \frac{\partial Q_s}{\partial \psi_s} \frac{\partial \psi_s}{\partial T} \right),$$  \hspace{1cm} (2)

because $V_g$ is constant. Here, $E_F$ is the Fermi level. From eq. (2)

$$\frac{\partial \psi_s}{\partial T} = - \frac{\partial E_F}{\partial T} \left( 1 + \frac{\varepsilon_i}{d_i e} \left( \frac{\partial Q_s}{\partial E_F} \right)^{-1} \right)^{-1}$$  \hspace{1cm} (3)

is obtained. In eq. (3) $\partial Q_s / \partial E_F \approx \partial Q_s / \partial \psi_s$ is used because the $E_F$ shift and $\psi_s$ variation have the same effect on $Q_s$ for $\psi_s > kT_c$, where $kT_c$ is the gradient of the localized state distribution which is assumed to be exponential with respect to the localized state energy. This relationship is verified in the appendix. Thus,
Fig. 2. Compensation factor $f_c$ vs Fermi level position at the a-Si:H/SiO$_2$ interface. The level density is assumed to be $2 \times 10^{16}$ cm$^{-3}$ eV$^{-1}$ at 0.7 eV below the conduction band and $T_c = 1200$ K.

Fig. 3. Structure of MOSFET used in the measurement.

The temperature dependence of the energy difference between the conduction band and the Fermi level at the interface

$$\Delta E = (E_c - E_F)_{\text{bulk}} - \psi_s$$

is compensated even if $E_F$ has a temperature dependence. $(E_c - E_F)_{\text{bulk}}$ is the energy difference between the conduction band and the Fermi level at the bulk. It should be noted that the degree of compensation depends on the SiO$_2$ thickness $d_i$.

The detailed analysis demonstrated in the appendix assuming an exponential localized state profile shows that

$$\frac{\partial \psi_s}{\partial T} = -\frac{1}{1 + a/d_i} \frac{\partial E_F}{\partial T} = -f_c \frac{\partial E_F}{\partial T}$$

$$a = \sqrt{2} \varepsilon / e \sqrt{\varepsilon_s g_s}$$

where $\varepsilon_s$ is the dielectric constant of a-Si:H and $g_s$ is the localized level density at the Fermi level of the a-Si:H/SiO$_2$ interface. The compensation factor $f_c = 1/(1 + a/d_i)$ is plotted as a function of $\Delta E$ of eq. (4) for the two SiO$_2$ thicknesses $d_i$ of 0.2 $\mu$m and 0.08 $\mu$m in fig. 2. It is assumed that the localized state density at 0.7 eV below the conduction band is $2 \times 10^{16}$ cm$^{-3}$ eV$^{-1}$ and $T_c = 1200$ K. It should be noted that the factor $f_c$ approaches unity when $\Delta E$ is reduced, i.e., $g_s$ becomes large, and that the factor is large for thick SiO$_2$. When $f_c = 1$, the statistical Fermi level shift at the bulk is completely compensated by the temperature dependence of $\psi_s$, and $\Delta E$ is temperature independent.
3. Experiment

The structure of the MOSFET used in the measurement is shown in fig. 3. The a-Si : H film was deposited by the conventional GD method onto SiO₂ films which were formed on the crystalline Si surface by thermal oxidation. The source and drain electrodes separated from each other by 10 μm were formed by Al evaporation onto a-Si : H film. Two kinds of samples whose SiO₂ thicknesses were 0.08 μm and 0.2 μm were prepared. As previously discussed, the degree of compensation of the statistical Fermi level shift caused by the temperature dependence of the surface band bending depends on the insulator film thickness. We therefore compared the temperature dependences of the conductivities of MOSFETs having different insulator film thicknesses.

The temperature dependence of the drain current was measured applying positive gate voltage. The drain voltage was 50 mV. Figure 4 shows the results for the sample whose SiO₂ thickness 0.2 μm. As can be seen the drain current increases and the activation energy decreases as a result of the positive gate voltage. These phenomena reflect the Fermi level shift toward the conduction band at the interface due to the field effect.

![Graph showing temperature dependence of drain current](image)

Fig. 4. Temperature dependence of the drain current at several gate voltages: the thickness of SiO₂ is 0.2 μm.
Samples were annealed each time before the drain current was measured. This is because the drain current was reduced gradually by the electric field and thermal stresses, when the gate voltage was applied at high temperature. This is probably due to carrier trapping at the interface [8] or to the drift of ions in a-Si: H resulting from the electric field. The reduction of the drain current by the electric and thermal stresses was recovered by annealing at 380 K for 1 h. The samples were then placed in the measurement temperature environment for 1 h. The data shown in fig. 4 were obtained by repeating this procedure.

We obtained an average conductivity $\sigma_{av}$ from the drain current as

$$\sigma_{av} = i_d L / V w d,$$

where $i_d$ and $V$ are drain current and the applied drain voltage. Additionally, $L$, $w$, and $d$ are channel length, channel width, and the thickness of a-Si: H respectively. This $\sigma_{av}$ is the average of the conductivity distributed throughout the depth of a-Si: H. The pre-exponential factor $\sigma_{0av}$ is obtained by extrapolation of $\sigma_{av}$ to $1/T = 0$.

$$\sigma_{av} = \sigma_{0av} \exp(-E_a / kT),$$

where $E_a$ is the activation energy of the temperature dependence of the drain current, and is almost equal to $\Delta E$ of eq. (4).

Fig. 5. Relationships between the pre-exponential factor of the average conductivity and the activation energy. The thicknesses of SiO₂ are 0.2 μm and 0.08 μm.
The relationships between $\sigma_{0av}$ and $E_a$ obtained from the samples whose SiO$_2$ thicknesses are 0.08 $\mu$m and 0.2 $\mu$m respectively, are plotted in fig. 5. It was found that the pre-exponential factors of conductivity are systematically varied with the activation energy for both samples. In the sample having a thick SiO$_2$ film, the pre-exponential factor is smaller and its activation energy dependence is weaker.

4. Discussion

The SiO$_2$ thickness dependence of $\sigma_{0av}$ shown in fig. 5 demonstrates the significance of the Fermi level statistical shift. In the MOSFET whose SiO$_2$ thickness is 0.2 $\mu$m, the statistical shift is considered to be nearly compensated by the temperature dependence of the surface band bending. This figure indicates that $\sigma_{0av}$ is reduced by the compensation effect. On the other hand, in the sample having thin SiO$_2$ film the effect of the statistical Fermi level shift is not sufficiently compensated when the gate voltage is small and $E_a$ ($\approx \Delta E$) is large (see fig. 2). When $E_a$ is reduced by the gate voltage, the degree of compensation increases because the compensation factor $f_c$ shown in fig. 2 approaches unity. Thus, the fact the $\sigma_{0av}$ of the MOSFET having thin SiO$_2$ rapidly decreases with $E_a$ also indicates that $\sigma_{0av}$ is reduced by the compensation of the Fermi level statistical shift.

The conductivity $\sigma_{av}$ is the average conductivity along the depth of a-Si : H. The relationship between $\sigma_{0av}$ and the activation energy shown in fig. 5 is influenced by the gate voltage dependence of the conducting layer thickness at the a-Si : H/SiO$_2$ interface. The pre-exponential factor of the conductivity unaffected by the statistical shift of the Fermi level should be obtained by the analysis of the conductivity of the MOSFET having thick SiO$_2$. This is because the effect of the statistical shift is nearly compensated for automatically by the temperature dependence of the surface band bending as previously discussed.

The average conductivity $\sigma_{av}$ is expressed as

$$\sigma_{av} = \frac{1}{d} \int_0^d \sigma(x) \, dx$$

$$= \frac{1}{d}\sigma_0 \exp\left(-\frac{(E_c - E_{F0})_{bulk}}{kT}\right) \int_\psi^0 \exp\left(\frac{\psi}{kT}\right) \frac{\partial x}{\partial \psi} d\psi,$$  \hfill (7)

where $\sigma(x)$ is the conductivity at depth $x$ and $d$ is the thickness of a-Si : H. $\sigma_0$ is almost equal to the pre-exponential factor at the a-Si : H/SiO$_2$ interface because the conductivity of the MOSFET is predominantly contributed by the interface. $(E_c - E_{F0})_{bulk}$ is the temperature independent part of the energy difference between the conduction band and the bulk Fermi level. That is, $E_{F0}$ is the Fermi level at 0 K. The factor $\partial \psi / \partial x$ is evaluated by solving a Poisson equation assuming the exponential localized state profile [9].
The integral of eq. (7) is calculated numerically. This numerical calculation contains three parameters to be determined. They are the localized state density $g_0$ at $E_{F0}$, the gradient $k T_c$ of the exponentially distributed localized state profile, and $(E_c - E_{F0})_{\text{bulk}}$. These parameters were determined so that the calculated gate voltage dependence of the activation energy of the conductivity is consistent with that experimentally measured. The determined parameters are $g_0 = 2 \times 10^{16}$ cm$^{-3}$ eV$^{-1}$ and $k T_c = 0.1$ eV, which are consistent with the results of the space charge limited current measurement [10] and $(E_c - E_{F0})_{\text{bulk}}$ estimated at 0.71 eV.

The pre-exponential factor $\sigma_0$ in eq. (7) is obtained by equating $\sigma_0$ with the experimentally observed average conductivity. The obtained $\sigma_0$ is plotted in fig. 6. The horizontal axis is the Fermi level position at the a-Si:H and SiO$_2$ interface. The error bar stems from the small discrepancy between the measured and calculated activation energies. The pre-exponential factor $\sigma_0$ shown in this figure is almost constant irrespective of the Fermi level position, and much smaller than that obtained from non-doped bulk a-Si:H conductivity [1].

If the effect of the statistical Fermi level shift at the bulk is eliminated by the MOSFET, the Meyer–Neldel rule is no longer observed. Therefore, it is concluded that the Meyer–Neldel rule, which is observed in the bulk a-Si:H conductivity, is caused by the statistical shift of the Fermi level. This conclusion is consistent with that of Beyer's experiment [6] in which the effect of the statistical Fermi level shift was eliminated by combining the temperature dependences of electric conductivity and thermopower.

Beyer's estimated $\sigma_0$, however, is greater than that shown in fig. 6. The reason for this discrepancy is not clear. The quality of the a-Si:H and SiO$_2$ interface may be responsible for the small $\sigma_0$ obtained by us. It should be noted, however, that the product $N_c e \mu_0$ and $\sigma_0$ obtained from a more detailed independent electron transport theory [5] are even smaller than the values shown in fig. 6. The product $N_c e \mu_0$ is 1.6 (Ω cm)$^{-1}$ for $N_c = 10^{19}$ cm$^{-3}$ and $\mu_0 = 1$ cm$^2$/Vs, and $\sigma_0$ estimated by Cohen et al. [5] is 4.4 (Ω cm)$^{-1}$. These
estimated values are consistent with $a_0$ shown in fig. 6 within the experimental error and the ambiguity of the parameters used in the theory.

5. Conclusion

The pre-exponential factor of the temperature dependence of the a-Si:H conductivity, which is not affected by the statistical shift of the Fermi level, was estimated using a MOSFET. The effect of the statistical shift of the Fermi level with the temperature can be compensated at the a-Si:H/SiO$_2$ interface because of the temperature dependence of the surface band bending in the MOSFET with thick insulator films (SiO$_2$). The estimated pre-exponential factor is much smaller than that obtained from the bulk conductivity, and the Meyer–Neldel rule is no longer observed. The Meyer–Neldel rule which is observed in bulk a-Si:H conductivity is caused by the statistical Fermi level shift with the temperature.

Appendix

Equation (5) is derived in this appendix. Let us assume an exponentially distributed localized state profile,

$$g(E) = g_0 \exp\left(\frac{E - E_0}{kT_c}\right), \quad \text{(A1)}$$

where $E_0$ is an arbitrarily defined energy in the gap and $g_0$ is the level density at $E_0$. The Poisson equation,

$$\frac{d^2 \psi}{dx^2} = \frac{e^2}{\varepsilon_s} \int_{E_F}^{E_F + \psi} g(E) \, dE, \quad \text{(A2)}$$

where $\psi$ is band bending at $x$ (see fig. 1) and $E_F$ is the Fermi level at the bulk, is integrated as

$$\left(\frac{d\psi}{dx}\right)^2 = 2(kT_c)^2 \frac{e^2}{\varepsilon_s} g_0 \exp \frac{E_F - E_0}{kT_c} \left( \exp \frac{\psi}{kT_c} - \frac{\psi}{kT_c} - 1 \right)$$

$$= F(\psi, E_F). \quad \text{(A3)}$$

From Gaussian law the charge $Q_s$ at the surface is represented as

$$Q_s = \frac{\varepsilon_s}{e} \sqrt{F(\psi_s, E_F)}. \quad \text{(A4)}$$

For $\psi_s > kT_c$

$$\frac{\partial Q_s}{\partial E_F} = \frac{\varepsilon_s}{2e} \frac{1}{kT_c} \sqrt{F(\psi_s, E_F)}$$

$$\approx \left( \frac{\varepsilon_s}{2} g_0 \exp \left( \frac{E_F - E_0 + \psi_s}{kT_c} \right) \right)^{1/2} = \frac{\partial Q_s}{\partial \psi_s}. \quad \text{(A5)}$$
The value of \( g_0 \exp((E_F - E_0 + \psi_s)/kT_e) = g_s \) is the localized level density at the Fermi level of the a-Si:H/SiO\(_2\) interface. Equation (5) is thus directly obtained from eq. (4) and eq. (A5).

References