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Electrooptic Effect of Water in Electric Double Layer at Interface of GaN Electrode

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We determined the Pockels constant of water in the electric double layer (EDL) at the GaN electrode interface. For a positive (negative) bias, the difference transmittance showed a blue (red) shift in the interference fringes in the visible. This was caused by a negative (positive) refractive index change both in the EDL of water and in the space charge layer (SCL) of the GaN. The latter was associated with the blue shift in the absorption edge in the UV due to the band population effect in the GaN. The voltage drops took place within the interfacial layer at a ratio of about 3 : 1 for the SCL vs EDL at the modulation frequency of $f = 20\,\mathrm{Hz}$, estimated from the frequency dependence of the impedance. The Pockels constant of water in the EDL was determined to be $r_{13} = 0.63 \times 100\,\mathrm{pm/V}$ for the GaN electrodes. This is three times smaller than that at the surface of the indium tin oxide (ITO) electrode.

Keywords: Pockels effect, electric double layer, water, electroabsorption spectroscopy, GaN, liquid–solid interface, space charge layer, refractive index, optical nonlinearity, band population effect

1. Introduction

When a voltage is applied to an electrode in aqueous solution, an electric double layer (EDL) with a-few-nanometer scale at the water–electrode interface is formed. In this layer, counter ions were found to be accumulated.[1)] Then, the voltage drop takes place mainly on the electrode interface, so that an extremely high electric field is concentrated there. In a previous study, we used the high electric field in the EDL formed on the surface of a 300-nm-thick indium–tin-oxide (ITO) electrode layer to determine the Pockels constants of water in the EDL to be $r_{33} = (2.5 \pm 0.6) \times 100\,\mathrm{pm/V}$ and $r_{13} = (2.0 \pm 0.3) \times 100\,\mathrm{pm/V}$, where pm is picometer.[2)] For the Pockels effect to occur, it is essential to break the centrosymmetry of water in the presence of the interface, but the microscopic mechanism for the effect is yet to be clarified.

As inferred from the experimental study on the orientation order of water molecules at the interface of the metal electrode (Ag for example[3)]), understanding of the interaction between water molecules and electrodes is the key to clarifying the mechanism. Presently, it is not certain whether the Pockels constants of water are universal constants irrespective of the electrode materials or specific ones dependent on them. To solve this issue, in the present work, we have studied the Pockels effects of water within the EDL on the electrodes made of n-type GaN thin film doped with Si on sapphire substrates.[4)]

GaN is attracting much attention because H_2 gas generation from aqueous solution by photoelectrolysis using a GaN electrode has been recently observed.[4)] GaN is a promising photocatalysing semiconductor for clean H_2 generation by solar power because it has a very low toxicity even if it is dissolved in a solution and shows considerable resistance to corrosion in aqueous solution. It is interesting to study the nonlinear optical effects of water in contact with the surface of photocatalysing semiconductors. In addition, since ITO is an oxide while GaN is a nitride, it is expected that differences in the interaction of water molecules with oxygen and nitrogen atoms on the electrode surfaces may affect the Pockels effect.

2. Experimental Methods

GaN electrodes were made of a Si-doped, n-type GaN layer of $2.3\,\mu\mathrm{m}$ thickness with a $1.7 \times 10^{17}\,\mathrm{cm}^{-3}$ carrier density, grown by metallorganic vapor-phase epitaxy on a sapphire substrate of 0.43 mm thickness with thin buffer layers in between. Two electrodes of $11 \times 5\,\mathrm{mm}^2$ were used, at one end of which an ohmic contact was formed with indium of $1 \times 5\,\mathrm{mm}^2$ in size.

Measurement was carried out by electric-field modulation spectroscopy.[5)] Figure 1 shows the measurement system. Two GaN electrodes were immersed in 0.1 M NaCl aqueous solution. By applying an AC voltage between the electrodes, the optical constants were changed within the interface between water and the electrodes, i.e., in the EDL of water and in the space charge layer (SCL) on the surface of GaN.[6)] The probe light from a Xe lamp was transmitted through one electrode, which was placed at a loosely focused beam position. The other electrode, which was grounded, should show the same magnitude of signal but the opposite sign (π phase shifted, because the polarity of the applied voltage is

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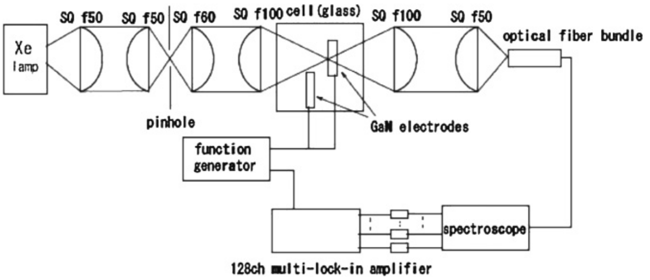

Fig. 1. Measurement system of electric-field modulation spectroscopy (top view). SQ f50 designates a quarz lens with a 50 mm focal distance. The probe light from the Xe lamp was collimated after being focused through a 400 µm pinhole.

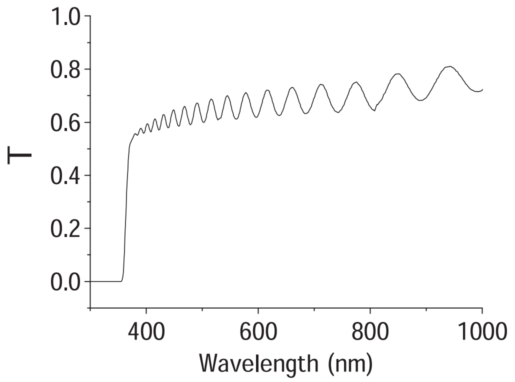

Fig. 2. Transmission spectrum of the 2.3-µm-thick GaN on the sapphire substrate placed in air. This was measured with the same wavelength resolution of 8 nm as in the electromodulation measurement.

opposite), so that if the probe light were transmitted through both electrodes, the signals cancel each other to yield zero signal unless there is some imbalance between the two electrodes. The electric-field-induced change in the transmittance was modulated at the AC frequency of f to be detected with a 128-channel lock-in amplifier.[7)] To focus the transmitted probe light onto the cross-sectional diameter of 0.5 mm on the input end of a (multimode-) fiber bundle connected to a monochromator, the spatial coherence of the probe was enhanced with a pinhole of 0.4 mm. For collimating and focusing the light, quartz lenses were used because the wavelength region of interest was as wide as 300–1000 nm. All the measurements were performed at room temperature.

3. Measurement Results

Figure 2 shows the transmittance spectrum of the GaN electrodes measured in air. The interference fringes are caused by the 2.3-µm-thick GaN layer. The decrease in the transmissivity in the UV region is due to the absorption above the bandgap energy of GaN. Figure 3 shows the normalized difference transmittance spectrum $\Delta T/T$ at the normal incidence. The AC voltage and the modulation frequency were 1 V (peak amplitude) and 20 Hz, respectively. There is a sharp increase in $\Delta T/T$ in the UV region, while there are interference fringes in the pattern of $\Delta T/T$ from the visible to near-IR regions. Figure 4 shows the normalized difference transmittance spectrum and the first derivative of the transmittance with respect to wavelength. This shows that the $\Delta T/T$ signal is caused by the wavelength shift in the interference fringes due to the electric-field-induced refractive index change.

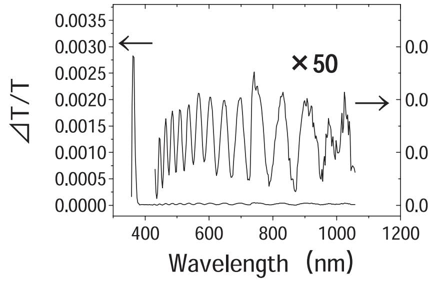

Fig. 3. Difference transmission spectrum normalized by the transmission spectrum for the GaN in 0.1 M NaCl aqueous solution at the incidence angle of $\theta = 0°$.

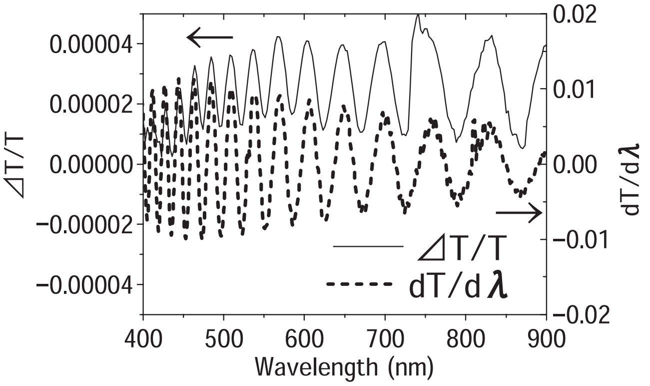

Fig. 4. Normalized difference transmittance spectrum (solid curve) and the first derivative of the transmittance with respect to wavelength (dashed curve).

4. Discussion

4.1 Origin of difference transmittance

The transmittance change in the visible to near-IR region is considered to be due to the change in the refractive index of water. However, there is also a possible contribution from the refractive index change of the GaN due to the band population effect.[8,9)] Figure 5 shows the band structure of an n-type semiconductor. The band structure near the interface bends to form an SCL by applying the voltage. As a result, the absorption edge shifts to the blue (red) side for the positive (negative) bias, leading to a sharp decrease in the absorption in the UV region. This phenomenon explains the sharp transmission increase in the UV region. The resulting change in the complex refractive index n_c in the SCL of GaN was evaluated using the Lorentz model, where the imaginary part of Δn_c was so determined that the observed net transmission change in the UV was reproduced. Under the Lorentz model, the real part of Δn_c is related to its

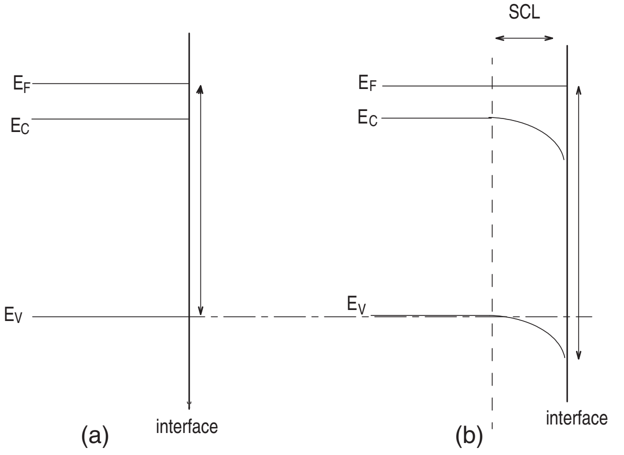

Fig. 5. Change in the band structure close to the surface in the n-type semiconductor caused by the band population effect (a) before and (b) after applying a positive voltage to the surface. E_c, E_v, and E_F are the lowest energy in the conduction band, the highest energy in the valence band, and the Fermi energy, respectively.

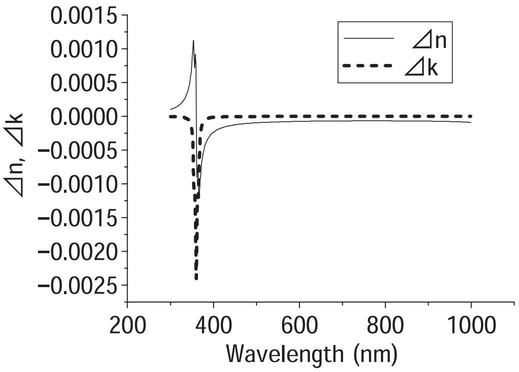

Fig. 6. Complex refractive index change in the SCL of GaN, assumed for reproducing the net transmittion change in the UV region in Fig. 3.

imaginary part through the Kramers-Kronig relations. Figure 6 shows the assumed complex refractive index change in the SCL in the GaN.

The difference transmittance was then calculated by the matrix method.[10)] The characteristic matrix of each layer was calculated by the optical constants of each layer, and that of the whole layers was readily calculated by the product of them. The water–electrode interface was assumed to be a multilayer system with a constant refractive index for each layer, as shown in Fig. 7. In fact, the refractive index varies continuously through the layers, but the simplest spatial distribution of the refractive index was employed for calculation. Presently, the lack of precise knowledge of the microscopic structure of the interfacial layers does not allow for more complex modeling of the spatial distribution. Before applying the voltage, the measured system is a three-layer structure of water, GaN layer, and substrate. After the voltage is applied, the system is considered to be composed of a five-layer structure of water, EDL, SCL, GaN layer, and substrate. As stated above, it was assumed that the refractive index changes uniformly at each layer. The dashed and thin solid curves in Fig. 8 show the results calculated with the refractive index change of water $\Delta n_w = 0$ and $\Delta n_w = -0.005$, respectively. Even with $\Delta n_w = 0$, there is an appreciable change in the interference fringes because of the refractive index change in the SCL of the GaN induced by the band population effect. However, the experimental (thick solid) curve cannot be reproduced well without a contribution of the refractive index change of water in the EDL as large as $\Delta n_w = -0.005$.

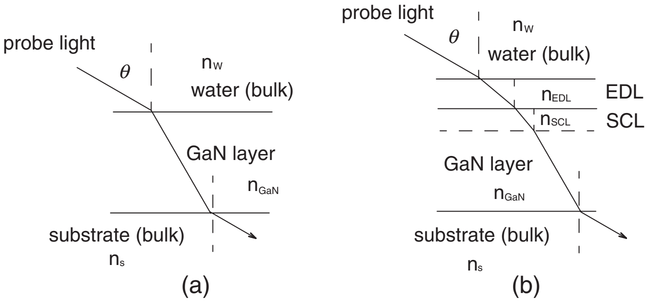

Fig. 7. Model of the interfacial layer: (a) three-layer and (b) five-layer structure before and after the voltage was applied, respectively.

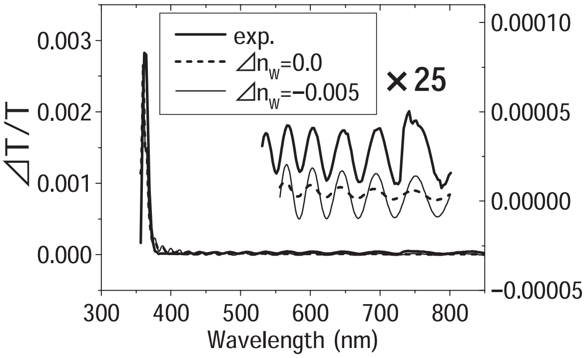

Fig. 8. Experimental (thick solid curve) and calculated results with refractive index change of water $\Delta n_w = 0$ (dashed curve) and $\Delta n_w = -0.005$ (thin solid curve).

There is residual discrepancy between the experimental and calculated results in two respects. One is that the experimental $\Delta T/T$ shows the net transmission change throughout the visible wavelength region while the calculated result does not. The other is a small difference in the wavelength dependence of the magnitude of the interference fringes. To explain these effects, a more complicated model is required.

4.2 *Voltage drop at interface*

To determine the Pockels constant, the electric field in the EDL should be estimated. The voltage drops in the interfacial layers were analyzed by the impedance measurement. Figure 9 shows a circuit system for the impedance

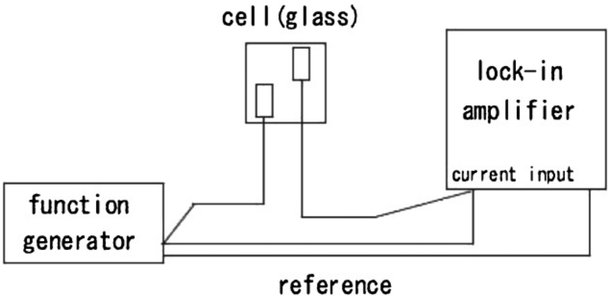

Fig. 9. Circuit system of impedance measurement (top view).

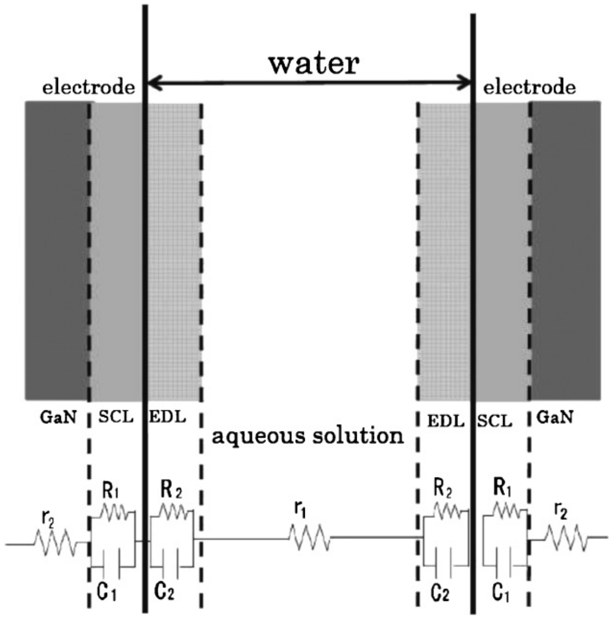

Fig. 10. Equivalent circuit for the measured system, which consists of interfacial layers, bulk GaN, and bulk solution. Since the two electrodes are equivalent, the circuit parameters are the same.

measurement. The geometrical positions of the electrodes in the cell and the concentration of NaCl were the same as those in Fig. 1. The AC voltage of $f = 930$ to 0.04 Hz was applied from a function generator and the resulting circuit current was measured using a lock-in amplifier. The impedance of the measured system is calculated using the formula:

$$Z' = \frac{X}{X^2 + Y^2} E \quad \text{and} \quad Z'' = \frac{-Y}{X^2 + Y^2} E, \tag{1}$$

where E, X, and Y are the externally applied AC voltage, and the real and imaginary parts of the signal current in the lock-in amplifier, respectively. Figure 10 shows the equivalent circuit for the interfacial layers, bulk GaN, and bulk solution. It was assumed to be composed of the serial circuit of the solution (resistence) and the thin layers of the SCL and EDL (parallel circuit of capacitance and resistance for each layer).[11] Then, the impedance of the equivalent circuit is given by

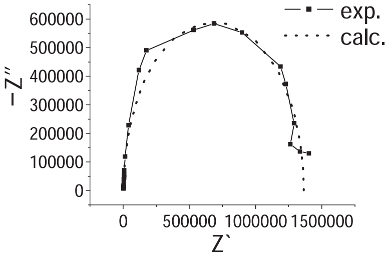

Fig. 11. Comparison between experimental (solid curve) and calculated (dotted curve) Cole–Cole plots.

$$Z' = \frac{2R_1}{1 + (\omega C_1 R_1)^2} + \frac{2R_2}{1 + (\omega C_2 R_2)^2} + r, \tag{2}$$

$$Z'' = -\frac{2\omega C_1 {R_1}^2}{1 + (\omega C_1 R_1)^2} - \frac{2\omega C_2 {R_2}^2}{1 + (\omega C_2 R_2)^2}, \tag{3}$$

with $\omega = 2\pi f$, where f is the frequency of the applied AC voltage, R_1 and C_1 are the resistance and capacitance in the parallel circuit for the SCL, R_2 and C_2 are those for the EDL, r_1 and r_2 are the resistance of the solution and the electrode, respectively, and $r = r_1 + 2r_2$. The impedance of each layer was estimated from the Cole–Cole plot of the frequency dependence of the impedance.[12] The dotted and solid curves in Fig. 11 show the calculated and experimental Cole–Cole plots, respectively. They indicate that the voltage drops took place within the interfacial layer at a ratio of 3 : 1 for SCL to EDL at the modulation frequency $f = 20$ Hz.

4.3 *Derivation of Pockels constant*

The pockels constant was determined from the refractive index change in water and the electric field in the EDL. In fact, the refractive index change is considered to be anisotropic, as represented by the refractive index ellipsoid,[2,5] such that

$$n_o = n_w - \frac{1}{2} n_w^3 r_{13} F, \tag{4}$$

$$n_e = n_w - \frac{1}{2} n_w^3 r_{33} F, \tag{5}$$

where n_o is the refractive index of the ordinary ray (the optical electric field E is parallel to the electrode surface while the external electric field F is normal to the surface), n_e is the refractive index of the extraordinary ray (both E and F are normal to the surface), n_w is the refractive index of bulk water, and r_{13} and r_{33} are the Pockels constants for the ordinary and extraordinary rays, respectively. The refractive index change of water was assumed to be wavelength independent. In this study, the measurement was performed only at the normal incidence, so that the Pockels constant of water in the EDL was determined only for the ordinary ray. It was thus determined to be $r_{13} = 0.63 \times 100$ pm/V for the GaN electrodes. This value is three times smaller than that for ITO. The Pockels constant for the extraordinary ray r_{33} is to be determined by measuring the dependence on the incidence angle in the future.

5. Conclusions

The Pockels effect of water in the EDL at the surface of the GaN electrode was observed. The value for the Pockels constant is three times smaller than that at the surface of the ITO electrode. This suggests that the Pockels effect of water in the EDL depends on the characteristics of the electrode surface where the EDL is formed.

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