Nondestructive and Quantitative Evaluation of a GaAs Epitaxial Layer Covered With a Silicon Nitride Insulating Thin Film After a Highly Accelerated Temperature and Humidity Stress With the Use of Photoreflectance Spectroscopy

Hideo Takeuchi, *Member, IEEE*

***Abstract*—We demonstrate that photoreflectance spectroscopic measurements of Franz-Keldysh oscillations are applicable to nondestructively quantify the changes in surface Fermi level and surface recombination velocity of semiconductors after reliability stress tests. The present sample, a two-layer homoepitaxial structure consisting of a top undoped GaAs epilayer and a bottom n-type GaAs epilayer, were initially covered with a silicon nitride insulating thin film. This sample was subjected to the highly accelerated temperature and humidity stress. Initially, we estimated the built-in electric field strength from the Franz-Keldysh oscillations. We found that the built-in electric field strength is enhanced after the acceleration stress. Next, we performed the numerical analysis of the built-in electric field strength as a function of probe-light power density. From the above-mentioned numerical analysis, we clarified that the surface recombination velocity of the top undoped GaAs epilayer is enhanced by a factor of two. In contrast, the surface Fermi level is hardly changed. We discuss this phenomenon from the viewpoint of the formation of the surface defects that enhance the surface recombination velocity.**

***Index Terms*—Reliability test, acceleration stress tests, highly accelerated temperature and humidity stress tests, semiconductor surface, insulating thin film, silicon nitride, passivation, surface recombination velocity, surface Fermi level, nondestructive evaluation, photoreflectance spectroscopy, Franz-Keldysh oscillations, GaAs, epitaxial layers.**

I. Introduction

It is wildly accepted that reliability tests are essential not only for commercial stage devices but also for developmental stage devices because device fabrication processes, which take account of the reliability, enables prompt research and development. For evaluating the reliability of the semiconductor devices, highly accelerated temperature and humidity stress tests (for simplicity referred as acceleration stress tests hereinafter) are usually used. We note that various researchers and device development groups often utilize the standard named "*Telcordia: Generic Reliability Assurance Requirements for Optoelectronic Devices Used in Telecommunication Equipment, GR-468 Issue Number 02 (2004)*". After the acceleration stress test, in usual, the device macroscopic characteristics change in current-voltage curves, breakdown thresholds and so on are investigated for improving the reliability. The macroscopic electrical characteristics are, of course, important. We emphasize that the macroscopic electrical characteristics connect with fundamental quantitative parameters reflecting semiconductor physics. Here, we focus our attention on insulating thin films covering semiconductor surfaces. The insulating thin films protect underlayers from humidity damages. The underlayers include semiconductor layers together with metal wiring layers. Compound semiconductors are generally fragile to the humidity, so that the less reliable insulating thin film affects device functions owing defects at the semiconductor surfaces induced by the humidity. In other words, the well-reliable insulating thin films enhance device functions. In the research and developmental field of high frequency electronic devices, the reliability of the insulating film is intensively investigated because the electrical characteristics of high-electron mobility transistors (HEMTs), heterojunction field effect transistors, and metal-insulator-semiconductor field effect transistors (MISFET) are sensitive to the surface covered with the insulating passivation film. Romero et al. reported that the use of N_2 plasma in HEMT passivation reduces current-collapse and gate-lag effects and that it prevents degradation of cut-off frequency $f_{\max}$ [1]. Shigekawa and Sugitani found from numerical calculation that passivation films with the designed stress play a crucial role in controlling the threshold voltages of $Al_xGa_{1-x}N$/GaN HEMTs [2]. Kikkawa et al. using a high-k Ta_2O_5 layer, optimized GaN-based MIS-HEMTs [3]. Liu et al. reported that, in a GaN-based MIS-HEMT, nitrogen passivation under a silicon nitride layer is effective to suppress the drain-current degradation in the presence of the high-electric-field stress for 40 hours [4]. The issue on the

Manuscript received 13 August 2022; revised 4 November 2022 and 12 November 2022; accepted 14 November 2022. Date of publication 16 November 2022; date of current version 8 March 2023.

The author is with the Division of Physics and Electronics, Osaka Metropolitan University, Osaka 558-8585, Japan, and also with the Faculty of Science and Technology, Sophia University Yotsuya Campus, Tokyo 102-8554, Japan (e-mail: Hideo.Takeuchi_PhD@omu.ac.jp; h-takeuchi-0s3@sophia.ac.jp).

Color versions of one or more figures in this article are available at https://doi.org/10.1109/TDMR.2022.3222783.

Digital Object Identifier 10.1109/TDMR.2022.3222783

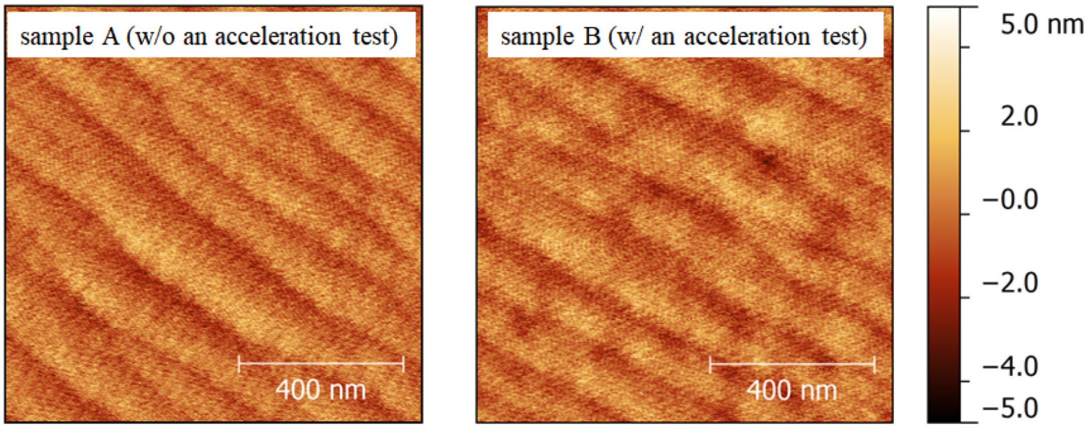

Fig. 1. AFM images of the silicon nitride film on samples A and B. The color bar corresponds to the surface roughness.

insulating film for passivation is not limited with the characteristics of high frequency compound semiconductor devices. In the solar cell, the insulating film also has a quite important role [5]. For example, LaPierre theoretically demonstrated that the insulating thin films improve current-voltage characteristics and efficiency of GaAs nanowire solar cells [6]. Hsu et al. found that Al_2O_3 serves as a good passivation layer for Cu(In,Ga)Se_2-based solar cells [7]. The above-mentioned improvements result from the suppression of surface recombination velocity [8]. The surface recombination velocity is enhanced by the increase in defects at the semiconductor surfaces. We also notice that the defects at the surface influence the phenomenon of the surface Fermi-level pinning [9]. The surface Fermi level relates to turn-on voltage of organic field effect transistors [10]. Accordingly, it is meaningful to test the reliability of the insulating thin film. Transmission electron microscopy (TEM) measurement is a useful tool to observe the interface between the insulating thin film and semiconductor layers after the acceleration stress test; however, it is impossible to quantify the change in the electronic characteristics from the observed TEM image. Accordingly, it is significant to explore how to quantify the change after the acceleration stress test.

In the present work, using photoreflectance spectroscopy [11], [12], [13], we nondestructively and quantitatively evaluated the change caused by the acceleration stress test for a GaAs epi-layer covered with a silicon nitride insulating thin film. In order to investigate whether the silicon nitride insulating thin film sufficiently protects the GaAs epilayer surface, it is fundamental to apply an appropriate monitoring sample. We used a two-layer homoepitaxial structure consisting of a top undoped GaAs epilayer and a bottom n-type GaAs epilayer. In the epitaxial structure, the undoped layer (i-layer) has a uniform built-in electric field that is sensitive to change in power density of probe light used the photoreflectance measurement [14]. We found that, after the highly accelerated temperature and humidity stress test, the surface recombination velocity of the top i-layer is strongly enhanced. In contrast, the surface Fermi level is hardly changed. We discuss the characteristics of the defects formed after the acceleration stress test.

II. Samples and Experimental Procedures

The present GaAs epitaxial structure consisting of the top i-layer (thicknesses: 200 nm) and the bottom n-layer (thicknesses: 3.0 μm; doping concentration: 3.0×10^{18} cm^{-3}) grown on a 2°-off (001)-oriented semi-insulating GaAs substrate by metal organic vapor phase epitaxy. The silicon nitride film, which was deposited on the i-layer, was grown by chemical vapor deposition, and its thickness was 30 nm. The highly accelerated temperature and humidity stress test was performed with the use of the following condition: humidity 70%; temperature: 393 K; total time of the acceleration stress test: 48 hours. We call the sample before the acceleration stress test as sample A and the sample after the acceleration stress test as sample B. Figure 1 shows the surface morphology of the silicon nitride thin film of samples A and B, where the surface image was taken with the use of atomic force microscopy (AMF). The AFM images apparently hardly differ. This means that the silicon nitride thin film itself was not damaged after the acceleration stress test. We estimated the built-in electric field strengths in the i-layer of samples A and B, using photoreflectance spectroscopy at room temperature. The pump light was the laser light with the wavelength of 532 nm chopped at the frequency of 630 Hz. The power density of the pump light was 80 mW/cm^2. The probe beam was obtained from a tungsten-halogen lamp dispersed by a monochromator with a 1.2-nm resolution. The power density of the probe light was varied from 2.8 to 30 μW/cm^2.

III. Experimental Results and Discussion

Figure 2(a) shows the photoreflectance spectra of samples A and B in the photon-energy range from 1.36 to 1.78 eV. The probe-light power density was set to be 30 μW/cm^2. The oscillation patterns, the so-called Franz-Keldysh oscillations, [11], [12], [13] starts from the fundamental transition energy of GaAs at room temperature. The appearance of the Franz-Keldysh oscillations clearly indicates the presence of the built-in electric field in the i-layer. The Franz-Keldysh oscillations appears in the relatively wide photon-energy range. This is because, in the i-layer, the impurities such as ionized donors or accepters, which damps the

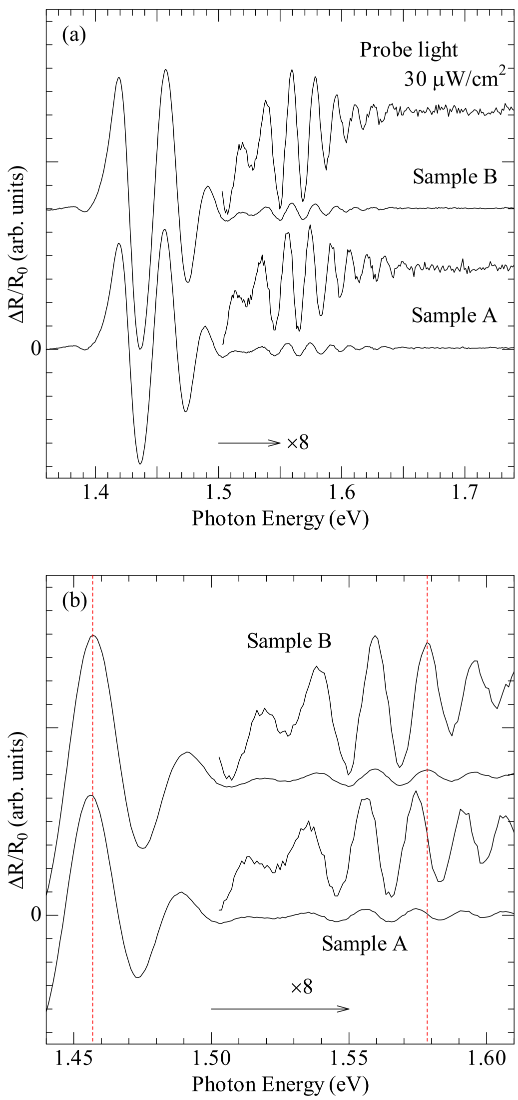

Fig. 2. Photoreflectance spectra at room temperature of sample A (w/o the acceleration stress test) and sample B (w/ the acceleration stress test). The probe-light power density was 30 μW/cm^2. (a) The spectra in the range from 1.36 to 1.78 eV. (b) The spectra in the range from 1.44 to 1.66 eV. For clarity, the spectra are vertically shifted. The dashed lines are guide for eyes, indicating difference in the peak position of the oscillation.

oscillation [15], [16], hardly exist. In other words, the present epitaxial structure is suitable for monitoring the effects of the acceleration stress test for the passivation ability of the insulating film. In order to highlight the change in the Franz-Keldysh oscillations between the two samples, we show the photoreflectance spectra in the photon-energy range from 1.44 to 1.66 eV in Fig. 2(b). The dashed line at 1.456 eV indicates that, in the two sample, the peak position of the Franz-Keldysh oscillations is located in the same photon energy. In contrast, the dashed line at 1.578 eV indicates the peak-position difference in the Franz-Keldysh oscillations between the two samples. The period of the Franz-Keldysh oscillations connects with the built-in electric field strength, so that the present phenomenon suggests that the built-in electric field strength is changed owing to the acceleration stress test. We reported in [14] that the built-in electric field strength is dominantly influenced both by the surface Fermi level and by the surface recombination velocity. Accordingly, the surface Fermi level or the surface recombination velocity is varied after the acceleration stress test.

In order to evaluate the effects of the acceleration stress test on the surface Fermi level and surface recombination velocity, initially, we estimated the built-in electric field strength of the two samples. We indexed the peaks and/or dips to the integer j from the fundamental transition energy and plotted the photon energy positions of in the spectra as a function of quasi-index ξ_j:

$$\xi_j = \left[\frac{3\pi}{4}\left(j - \frac{\phi}{\pi}\right)\right]^{3/2}. \quad (1a)$$

$$\phi = \frac{\pi}{2} + \delta. \quad (1b)$$

Here, the quantity ϕ is the phase term [14], [17], [18], which reflects the interference effect caused by the presence of the insulating thin film. The quantity ϕ in (1b) is the multiplication of the probe-light wavenumber and the optical path length in the silicon nitride thin film. In the present samples, the silicon nitride film covers the i-layer, so that the interference effect leading to δ is not negligible. The phase term ϕ, therefore, should be taken into account for precisely estimating the built-in electric field strength. Equation (1a) is equivalent to the theory by Aspnes and Studna [19] in the case where the interference-effect factor δ is zero corresponding to the absence of the interference effect. The applied refractive index of the silicon nitride thin film was 2.05 to derive the interference-effect factor δ [20]. The obtained plots are shown in Fig. 3, where the probe-light power density was 30 μW/cm^2. The closed and open circles are the peak and dip photon energy of the Franz-Keldysh oscillations of samples A and B, respectively. It is apparent that the plots show a linearity, indicating that the uniform built-in electric field strength is formed in the i-layer of each sample. The slope, the electro-optic constant $\hbar\Theta$, is given as a function of built-in electric field strength F [19].

$$(\hbar\Theta)^3 \equiv \frac{e^2\hbar^2F^2}{2\mu}. \quad (2)$$

Here, the quantity μ is the reduced effective mass. In GaAs, the value is estimated to be 0.0556 in units of the electron mass in a vacuum [21]. We fitted the following equation to the peak and dip photon energy values $\hbar\omega_j$ (closed and open circles),

$$\hbar\omega_j = (\hbar\Theta)\xi_j + E_0 \quad (3)$$

where the quantity E_0 is the fundamental transition energy of GaAs. The fitting results are depicted as the solid lines. The fitted solid lines agree with the experimental value. In addition, the two solid lines converge at the intercept E_0 of 1.425 eV. The value of 1.425 eV is almost the same as the fundamental transition energy of GaAs (1.424 eV) at room temperature [22]. This indicates that the present fitting analysis has reasonable precision.

Finally, we estimate the surface Fermi level ΔE_F and surface recombination velocity S, where the reference point of ΔE_F is a mid-gap level of GaAs. The built-in electric field strength is enhanced as the probe-light power density is decreased. This

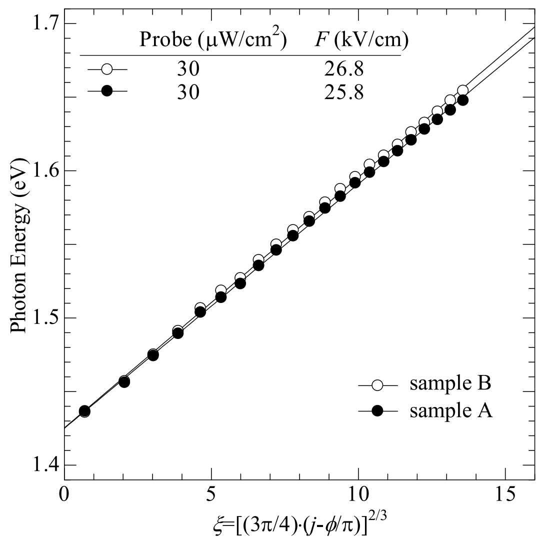

Fig. 3. Peak and dip photon energies of the Franz-Keldysh oscillations as a function of quasi-index ξ_j. The closed and open circles are the peaks and dips of the Franz-Keldysh oscillations of samples A and B, respectively, and the solid lines correspond to the fitted results using (3).

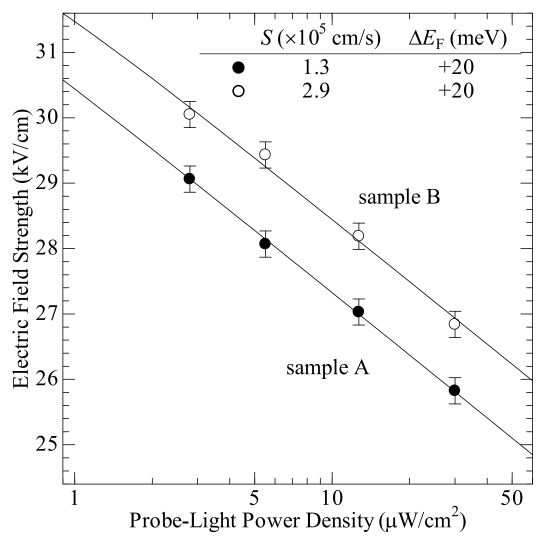

Fig. 4. The estimated built-in eclectic field strength F (closed and open circles) plotted as a function of probe-light power density. The solid lines are obtained by numerically calculation using the computational simulation software PC-1D developed on the basis of the theory in [24].

originates from the reduction of the screening effect of the probe light on the built-in surface electric field [14], [23]. The solid lines are obtained by the numerical calculation using the software PC-1D developed on the basis of the theory proposed in [24]. The theory is based on the Boltzmann-Poisson model. The material parameters, which were used in the present calculation, are the same as those in [14]. The solid line has a linear slope in the semi-logarithmic plot in Fig. 4. We reported that this result indicates the surface Fermi level ΔE_F is located almost at the mid-gap of GaAs [14]. The estimated surface Fermi levers are +20 meV in both samples A and B. In contrast, the solid line is shifted up in sample B subjected to the acceleration stress test. This means that the surface recombination velocity is enhanced, according to [14]. The surface recombination velocities S are estimated from the numerical calculation to be 1.3×10^5 cm/s for sample A and 2.9×10^5 cm/s for sample B. This indicates that the present acceleration stress test enhances the surface recombination velocity by a factor of two.

Here, we discuss the enhancement of the surface recombination velocity owing to the present highly accelerated temperature and humidity stress test. The surface recombination velocity S is enhanced by the presence of the surface defect states, as pointed out in [14]. As shown in Fig. 1, the silicon nitride thin film is hardly changed after the acceleration stress test. Accordingly, the degradation of the silicon nitride film is not a responsible factor. We, therefore, have reached the following conclusion: The water molecule penetrates the relatively robust silicon nitride film. The water molecule triggers producing the surface defects by the assist of the relatively high temperature. We also note that the surface Fermi level ΔE_F hardly is changed. This means that the surface levels formed by the defects are mainly located at the mid-gap of GaAs.

IV. Conclusion

We have explored the feasibility that photoreflectance spectroscopy is applicable to quantitatively evaluate the GaAs epilayer covered with the silicon nitride thin film after the highly accelerated temperature and humidity stress test. We have analyzed the Franz-Keldysh oscillations appearing in the photoreflectance spectra and estimated the built-in electric field strength. We have found that the built-in electric field strength in the *i*-layer is enhanced by the acceleration stress test. We have compared the built-in electric field strength dependence on the probe light power density with the numerical simulation. It has been clarified that the surface recombination velocity of 1.3×10^5 cm/s is enhanced to be 2.9×10^5 cm/s after the acceleration stress test. We have attributed the origin of the present phenomenon to the reasonable assumption that the water molecule penetrates the silicon nitride film and produces the surface defects by the assist of the relatively high temperature. The present findings demonstrate that the photoreflectance spectroscopy is applicable to contactless and quantitative evaluation of the surfaces of semiconductor devices subjected to the acceleration stress test.

References

[1] M. F. Romero et al., "Effects of N_2 plasma pretreatment on the SiN passivation of AlGaN/GaN HEMT," *IEEE Electron Device Lett.*, vol. 29, no. 3, pp. 209–211, Mar. 2008.

[2] N. Shigekawa and S. Sugitani, "Numerical analysis of impact of stress in passivation films on electrical properties in AlGaN/GaN heterostructures," *IEICE Electron. Exp.*, vol. 6, no. 14, pp. 1045–1050, 2009.

[3] T. Kikkawa, K. Imanishi, N. Hara, H. Shigematsu, and K. Joshin, "Recent progress of GaN electronic devices for wireless communication system," in *Proc. SPIE*, 2008, Art. no. 68941Q.

[4] S.-C. Liu, B.-Y. Chen, Y.-C. Lin, T.-E. Hsieh, H.-C. Wang, and E. Y. Chang, "GaN MIS-HEMTs with nitrogen passivation for power device applications," *IEEE Electron Device Lett.*, vol. 35, no. 10, pp. 1001–1003, Oct. 2014.

[5] G. Dingemans and W. M. M. Kessels, "Status and prospects of Al_2O_3-based surface passivation schemes for silicon solar cells," *J. Vac. Sci. Technol. A*, vol. 30, no. 4, 2012, Art. no. 40802.

[6] R. R. LaPierre, "Numerical model of current-voltage characteristics and efficiency of GaAs nanowire solar cells," *J. Appl. Phys.*, vol. 109, no. 3, 2011, Art. no. 34311.
[7] W.-W. Hsu et al., "Surface passivation of Cu(In,Ga)Se_2 using atomic layer deposited Al_2O_3," *Appl. Phys. Lett.*, vol. 100, no. 2, 2012, Art. no. 23508.
[8] D. E. Aspnes, "Recombination at semiconductor surfaces and interfaces," *Surf. Sci.*, vol. 132, nos. 1–3, pp. 406–421, 1983.
[9] H. H. Wieder, "Surface fermi level of III–V compound semiconductor-dielectric interfaces," *Surf. Sci.*, vol. 132, nos. 1–3, pp. 390–405, 1983.
[10] K. P. Pernstich et al., "Threshold voltage shift in organic field effect transistors by dipole monolayers on the gate insulator," *J. Appl. Phys.*, vol. 96, no. 11, pp. 6431–6438, 2004.
[11] F. H. Pollak and H. Shen, "Modulation spectroscopy of semiconductors: Bulk/thin film, microstructures, surfaces/interfaces and devices," *Mater. Sci. Eng. R, Rep.*, vol. 10, nos. 7–8, pp. 275–374, 1983.
[12] H. Shen and M. Dutta, "Franz–Keldysh oscillations in modulation spectroscopy," *J. Appl. Phys.*, vol. 78, no. 4, pp. 2151–2176, 1995.
[13] R. Kudrawiec and J. Misiewicz, *Optical Modulation Spectroscopy in Semiconductor Research: Experimental Technique*, A. Patanè and N. Balkan, Eds. Berlin, Germany: Springer, 2012, ch. 4.
[14] H. Takeuchi, Y. Kamo, Y. Yamamoto, T. Oku, M. Totsuka, and M. Nakayama, "Photovoltaic effects on Franz–Keldysh oscillations in photoreflectance spectra: Application to determination of surface Fermi level and surface recombination velocity in undoped GaAs/*n*-type GaAs epitaxial layer structures," *J. Appl. Phys.*, vol. 97, no. 6, 2005, Art. no. 63708.
[15] D. E. Aspnes, "Electric field effects on the dielectric constant of solids" *Phys. Rev.*, vol. 153, no. 3, pp. 972–982, 1967.
[16] D. E. Aspnes, "Band nonparabolicities, broadening, and internal field distributions: The spectroscopy of Franz–Keldysh oscillations," *Phys. Rev. B, Condens. Matter*, vol. 10, no. 10, pp. 4228–4238, 1974.
[17] H. Takeuchi, Y. Yamamoto, R. Hattori, T. Ishikawa, and M. Nakayama, "Interference effect on the phase of Franz–Keldysh oscillations in GaAs/AlGaAs heterostructures," *Jpn. J. Appl. Phys.*, vol. 42, no. 11R, pp. 6772–6778, 2003.
[18] H. Takeuchi, Y. Yamamoto, and M. Nakayama, "Nondestructive determination of layers producing Franz–Keldysh oscillations appearing in photoreflectance spectra of heterojunction bipolar transistor structures based on their line-shape analysis," *J. Appl. Phys.*, vol. 96, no. 4, pp. 1967–1974, 2004.
[19] D. E. Aspnes and A. A. Studna, "Schottky-barrier electroreflectance: Application to GaAs," *Phys. Rev. B, Condens. Matter*, vol. 7, no. 10, pp. 4605–4624, 1973.
[20] S. M. Sze and K. K. Ng, *Physics of Semiconductors*, 3rd ed. Hoboken, NJ, USA: Wily, 2007, p. 791.
[21] D. F. Nelson, R. C. Miller, C. W. Tu, and S. K. Sputz, "Exciton binding energies from an envelope-function analysis of data on narrow quantum wells of integral monolayer widths in $Al_{0.4}Ga_{0.6}As$/GaAs," *Phys. Rev. B, Condens. Matter*, vol. 36, no. 15, pp. 8063–8070, 1987.
[22] O. Madelung, *Semiconductors—Basic Data*, 2nd ed. Berlin, Germany: Springer, 1996, p. 101.
[23] H. Shen et al., "Photoreflectance study of surface fermi level in GaAs and GaAlAs," *Appl. Phys. Lett.*, vol. 57, no. 20, pp. 2118–2120, 1990.
[24] P. A. Basore, "Numerical modeling of textured silicon solar cells using PC-1D," *IEEE Trans. Electron. Devices*, vol. 37, no. 2, pp. 337–343, Feb. 1990.

Hideo Takeuchi (Member, IEEE) was born in Shiga, Japan, in 1973. He received the B.S. degree in engineering from Osaka City University, Osaka, Japan, in 1995, the M.S. degree in physics from the Graduate School of Science, Osaka University in 1997, and the Ph.D. degree in engineering from the Graduate School of Engineering, Osaka City University in 2002.

From 1997 to 1999, he was an Engineer for Si-based LSI Technology with ROHM Company Ltd., Kyoto, Japan. From 2002 to 2008, he was with Mitsubishi Electric Corporation, Hyogo, Japan, where he was engaged in the research and development of high frequency electronic devices. He focused his attention on the characterization and design technology of epitaxial wafers for heterojunction bipolar transistors and $Al_xGa_{1-x}N$/GaN-based high-electron-mobility transistors. From 2008 to 2013, he was an Associate Professor with the Department of Electronic Systems Engineering, School of Engineering, The University of Shiga Prefecture, Shiga. Since 2013, he has been an Associate Professor with the Department of Applied Physics, Graduate School of Engineering, Osaka City University. In addition, since 2017, he has also been a Collaborate Researcher with the Faculty of Science and Technology, Sophia University, Tokyo, Japan. In the academic position of the universities, he has been focusing his attention on optical functions of semiconductors. In April 2022, Osaka Prefecture University and Osaka City University united to form the Osaka Metropolitan University. Accordingly, since 2022, he has been also an Associate Professor with the Division of Physics and Electronics, Graduate School of Engineering, Osaka Metropolitan University. His research interests include terahertz radiation phenomena observed with the use of the time-domain techniques, ultrafast spectroscopy, photoreflectance spectroscopy, inspection technology for compound semiconductor wafers, and excitons in semiconductors. He is a member of the Physical Society of Japan, the Japan Society of Applied Physics, the American Physical Society, the Institute of Electrical and Electronics Engineers, the American Vacuum Society, OPTICA, (formerly the Optical Society of America, OSA), and the Institute of Physics.