Chapter 3

# Highly Sensitive Singlet Oxygen Spectroscopic System Using InGaAs PIN Photodiode

Iwao Mizumoto, Hiroshi Oguma and Yostumi Yoshi

Additional information is available at the end of the chapter

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**Abstract**

The spectrum of $^1O_2$ was measured by the InGaAs photodiode for an optical communication system with charge integration amplifier (InGaAs-CIA). The photo-excited current is charged in photodiode junction capacitance itself. The current is changed to the voltage about $10^{12}$ times without feedback resistance. The minimum detectable power of InGaAs CIA system with liquid nitrogen was achieved 0.1 fW of 10 sec integration time at the wavelength of 1.28 μm. The optical band pass filter-based system for ultra–low-level light detection was succeeded in spectrum measurement of $^1O_2$ by 13-LOOH with cytochrome c. The 8 channel InGaAs-CIA array system enables to achieve optical multichannel detection for ultra-low level light at $10^{-13}$ W from $10^{-15}$ W level in the near-infrared region. The optical resolution was about 200 nm by 1 channel. The spectrum of $^1O_2$ by mixing NaOCl and $H_2O_2$ was demonstrated. The shape of spectrum by $^1O_2$ was matched to that of measured by the spectrometer. The system was succeeded in instantaneous $^1O_2$ spectrum measurement without moving the wavelength dispersion device. The generation of $^1O_2$ by photo-excited Rose Bengal was fabricated to develop food antioxidant chemistry or source reagent of cosmetic product. The system uses super luminosity LED for excitation light source and InGaAs CIA. The $^1O_2$ generation will be controlled by the InGaAs-CIA monitoring system. The system will be used in the chemical plant of primary material production.

**Keywords:** InGaAs PIN photodiode, low-level light, singlet oxygen, charge integrating amplifier, spectroscopic system, multichannel, filter based, Rose Bengal

## 1. Introduction

Low-level light is emitted from various kinds of faint sources in the visible region. It is difficult to specify the emitting source chemically because the spectra overlap each other. In the near infrared (NIR), existence of the substance of biological material for emitting is not scarce,. Also the thermal back ground noise is exceedingly released compared with the middle-infrared region or the far-infrared region. The problem of measuring exceedingly low levels light from various kinds of faint sources is of considerable interest and importance. Especially, $^1O_2$ is emitted with low-level light at the 1.27 μm of NIR optical band. $^1O_2$ is one of active oxygen species from the biological material. The chemiluminescent substance is scarce at the NIR region, the use of spectroscopic $^1O_2$ emission will be available as a chemical and physical analytical tool in. There are many biochemists, pathologists, and agricultural chemists who focus on such a weak optical signal in the NIR [1]. Since silicon photodiode have no optical sensitivity in the NIR, Ge PIN photodiodes with phase sensitive amplifier are used in NIR [1]. Johnson noise is given by the equation, Eq. (1),

$$I_j = \sqrt{\frac{4 k_D T_n}{R_{sh}}} \tag{1}$$

where $I_j$ is thermal noise current, $k_D$ is Boltzmann constant, $T_n$ is temperature in kelvin, $R_{sh}$ is shunt resistance in photodiode. $R_{sh}$ is in inverse proportion to dark current. The shot noise (dark) is given by the next equation, Eq. (2),

$$I_{sD} = \sqrt{2e I_{dn}} \tag{2}$$

where $I_{sD}$ is shot noise in darkness, $e$ is the electron charge, $I_{dn}$ is the dark current. At the operating temperature of 77 K, the device thermal noise and shot noise are not dominant [2, 3, 4]. The optical sensitivity is mainly decided by the dark current. The principal noise current of such a detector with a transimpedance amplifier (TIA) is given by the equation, Eq. (3),

$$I_n = \sqrt{I_{dn} e \Delta f} \tag{3}$$

where $I_n$ is noise current, $I_{dn}$ is dark current, $e$ is the electron charge, and $\Delta f$ is the bandwidth. **Figure 1** shows the temperature dependence of the dark current InGaAs photodiode (Fujitsu FID13Y23WY) and Ge PIN photodiode (Fujitsu FID13R53WZ) for the optical communication system. The dark current of an InGaAs photodiode at 77 K is three orders of magnitude less than of a Ge PIN photodiode.

**Figure 2** shows temperature dependence of quantum efficiency the InGaAs photodiode and the Ge PIN photodiode. The quantum efficiency of the Ge PIN photodiode decreases from the temperature of liquid nitrogen. That of the InGaAs maintains to the temperature of liquid helium. The dark current and quantum efficiency of the Ge PIN photodiode decrease in

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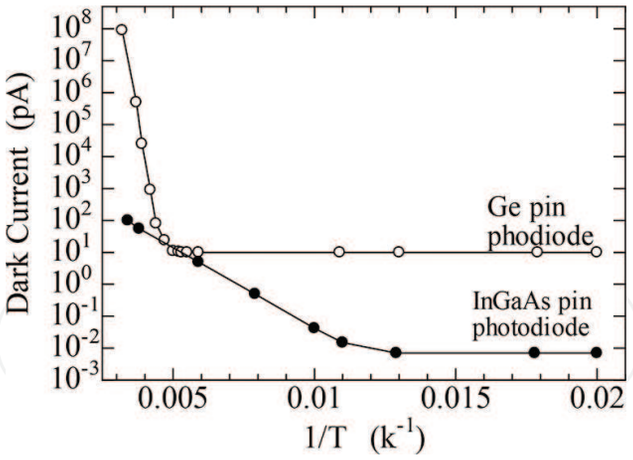


**Figure 1.** Temperature dependence of dark current InGaAs photodiode and Ge pin photodiode (identical to the one published in authors' previous work [5]).

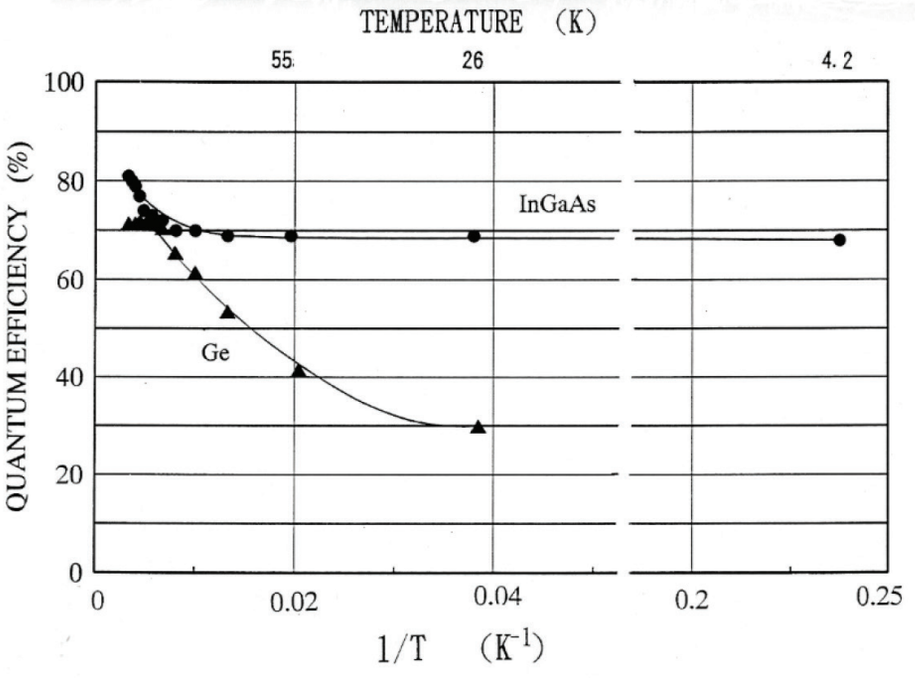


**Figure 2.** Temperature dependence of quantum efficiency InGaAs photodiode and Ge pin photodiode.

proportion to the device temperature. The device temperature of the InGaAs PIN photodiode has little influence to the quantum efficiency. Therefore, the InGaAs PIN photodiode is more suitable than the Ge PIN photodiode for detecting low-level light in the NIR region.

## 2. Circuit of detection system

The impedance of an InGaAs PIN photodiode cooled to 77 K is so high (100 TΩ). It can be operated with a charge integrating amplifier (CIA) [2, 4, 5]. The amount accumulated charge

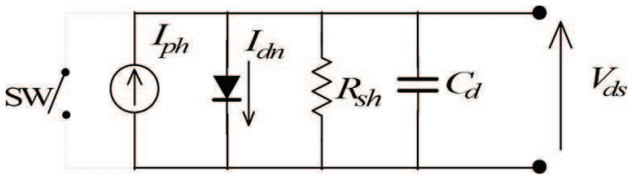


**Figure 3.** Diode equivalent circuit (identical to the one published in authors' previous work [5]).

in this configuration is directly measured as voltage. The photocurrent or carrier in the CIA is converted to voltage through the capacitance of a photodiode. **Figure 3** shows the diode equivalent circuit with a simplified signal source. $R_{sh}$ is so high and $I_{dn}$ is very small at the temperature 77 K.

The CIA output voltage is given by the next equation, Eq. (4).

$$V_{ds} = \frac{\int_0^\tau I_{ph}\, dt}{C_d} \tag{4}$$

Where $V_{ds}$ is the voltage of the signal output. $I_{ph}$ is the photocurrent, $\tau$ is integration time, $C_d$ is the capacitance of the detector. The InGaAs-CIA enables photocurrent to the voltage without a feedback register. The minimum detectable incident power is given by

$$P_{min} = \frac{h\nu}{\eta}\left[\frac{e_{am}\sqrt{\Delta f}}{e\tau} C_d + \sqrt{\frac{I_{dn}}{2e\tau}}\right] \tag{5}$$

Where $P_{min}$ is the minimum detectable power, $I_{dn}$ is the dark current, $e$ is the electron charge $\eta$ is the quantum efficiency of the photodiode, $\Delta f$ is the bandwidth, $e_{am}$ is the noise voltage of the amplifier, $\tau$ is the integration time, and $C_d$ is the capacitance [5]. At the condition $I_{dn} = 5 \times 10^{-15}$ A, $\eta = 0.7$, $C_d = 30$ pF, $e_{am} = 100$ nVHz$^{-1/2}$, $\tau = 10$ sec, $\Delta f = 100$ Hz, the calculated $P_{min}$ value is $6 \times 10^{-17}$ W.

**Figure 4** shows the InGaAs-CIA detailed circuit diagram. The InGaAs PIN photodiode (Fujitsu FID13Y23WY) was used for CIA. The output voltage measured an amount of photocurrent. A dual n-channel J. FET (2N6483) differential amplifier minimized current drift error from fluctuation of the temperature. The FET source follower circuit reduces the output impedance for reduction of inductive noise. The timer IC (NE555) with p-channel MOSFET (3SJ11A) controls the time of charge accumulating.

**Figure 5** shows the chart records of the InGaAs-CIA. The integration time of 10 sec yields differential voltage of 130 mV between on-emission light of $10^{-15}$ W and off light. The voltage fluctuation in 10 sec was 10 mV. The minimum detectable power was measured by the LED optical source (ADVANTEST TQ-28 at 1.28 μm with FWHM 30 nm) and attenuates NIR ND filters. The system obtained minimum detectable optical power $10^{-16}$ W at 1.28 μm with 10 sec. The result corresponded to the predicted value of equation.

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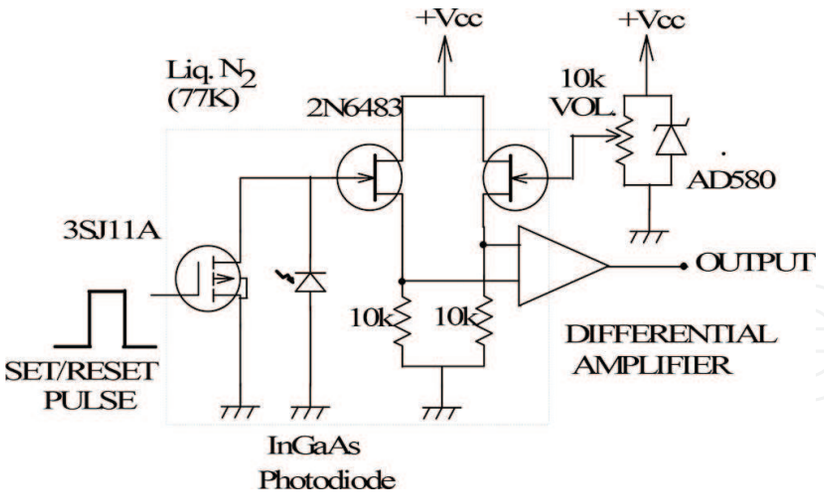


**Figure 4.** Circuit diagram of the InGaAs-CIA (almost identical to the one published in authors' previous work [5, 6]).

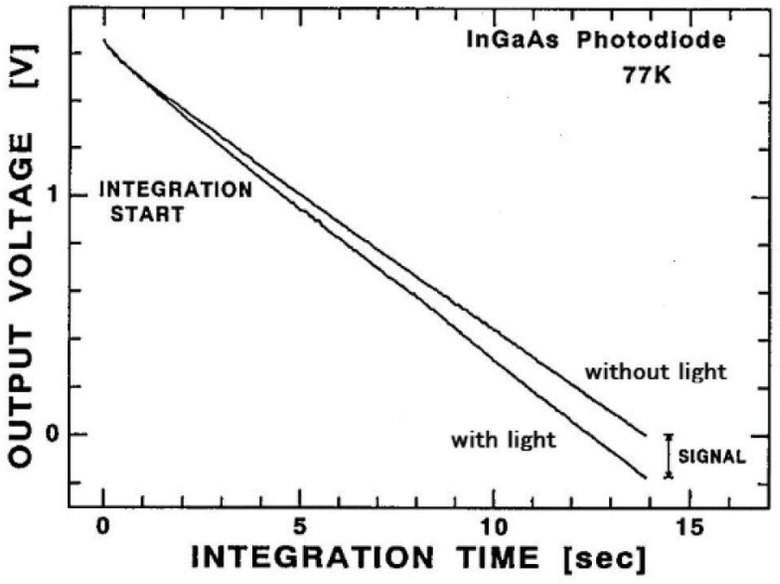


**Figure 5.** Chart records of the InGaAs-CIA (identical to the one published in authors' previous work [5]).

**Figure 6** shows the theoretical and experimental results of the minimum detectable power. The solid and dashed lines show the experimental and theoretical results, respectively. The minimum detectable power of $10^{-16}$ W was achieved at 1.28 μm wavelength.

At the theoretical line above 10 sec, the measured minimum detectable power was saturated. The influence of electrical FET device noise, 1/*f* low frequency noise, the saturation capacity of the dark current, and leak photocurrent are considered.

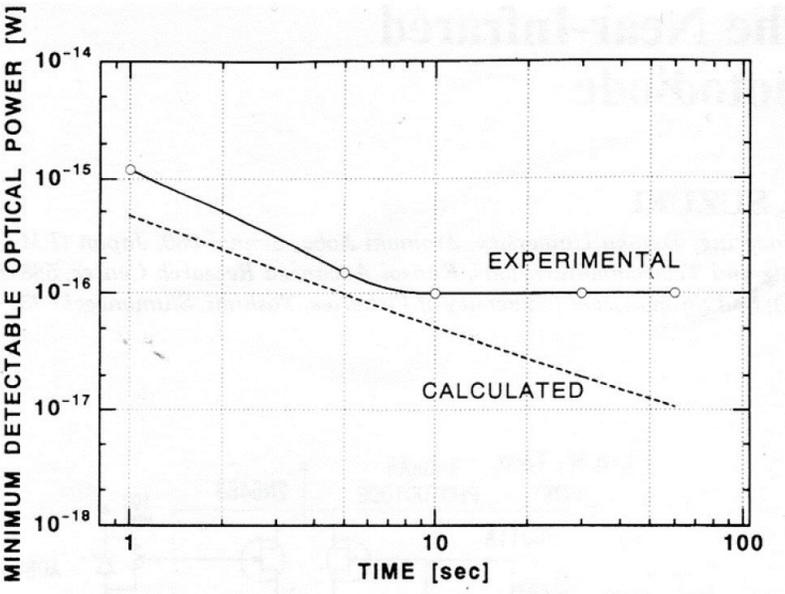


**Figure 6.** Minimum detectable power dependence of integration time (InGaAs pin photodiode at 77 K) (Identical to the one published in authors previous work [5]).

## 3. Application system of spectroscopic measurements in NIR

### 3.1. Filter-based high efficiency spectroscopic system

In the NIR region, low-level light has important information of biological, biochemistry, agricultural chemistry, and photochemistry. The emission phenomenon or spectrum is expected to explain the emission mechanisms. The biophoton or biological emission has extremely low-level light. The spectrum of the emission has broadly wavelength. The change of emission intensity is at a slow speed. An InGaAs-CIA is effective to accumulate excited photocurrent of the emission. It is difficult to focus for the spectrometer by lenses as the solid angle of biophoton or chemiluminescence from the living organism substance has a great angle of radiation and incoherent characteristic. Normally, the transmission of the spectrometer is less than 10%. A great solid angle as possible and short distance between optical source and dispersive element is important for the effective measurement. From these points of view, a high-efficiency filter-based InGaAs-CIA spectroscopic system was fabricated [6]. **Figure 7** shows a schematic diagram of the system. Fifteen interference filters (vacuum optics corporation of Japan) was used of the spectroscopic system. The measurement spectra range of the system has 1.0– 1.6 μm with 30–35 nm optical resolution. The interference filters have the average transmission of 82 ± 6%.

We measured the emission spectrum of $^1O_2$ at 1.27 μm to test the performance for our filter-based spectrometer. The emission with $^1O_2$ is very weak because it derives from a forbidden transition. The spectrum of $^1O_2$ produced by 13-LOOH (2 mM) with cytochrome c (10 μM), $NH_3$-$NH_4Cl$ (0.04 M), $D_2O$ is shown in **Figure 8**. We have observed a derivation biochemistry emission spectrum of $^1O_2$ produced by this reaction. It means that $^1O_2$ generated by oxidized 13-LOOH with cytochrome c of protein material of human body. The reaction is known as Russell's mechanism [7, 8].

**Figure 9** shows Russell's mechanism. The chemical equation is shown in Eq. (**6**).

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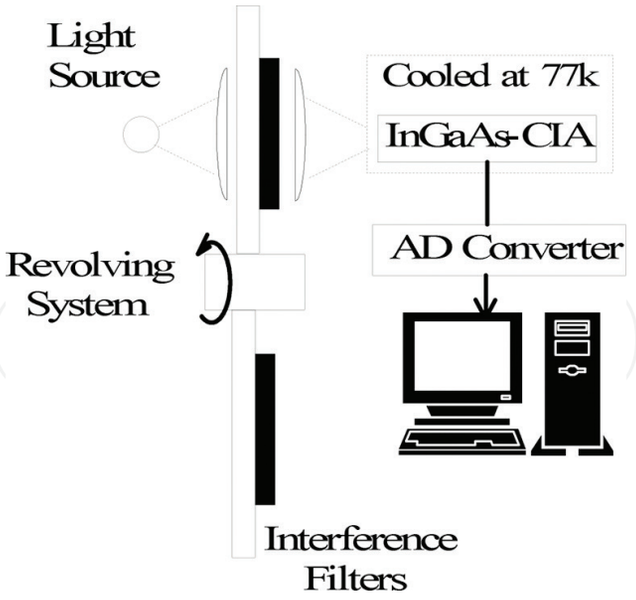


**Figure 7.** Interference filter based spectroscopic system (identical to the one published in authors' previous work [6]).

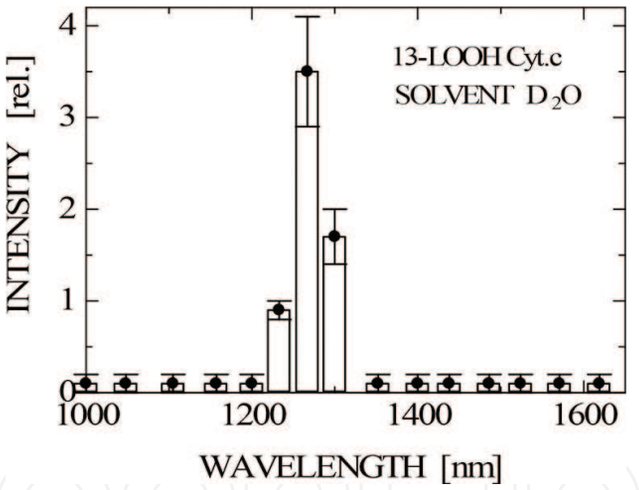


**Figure 8.** $^1O_2$ spectral of 13-LOOH with cytochrome c, $D_2O$ (identical to the one published in authors' previous work [6]).

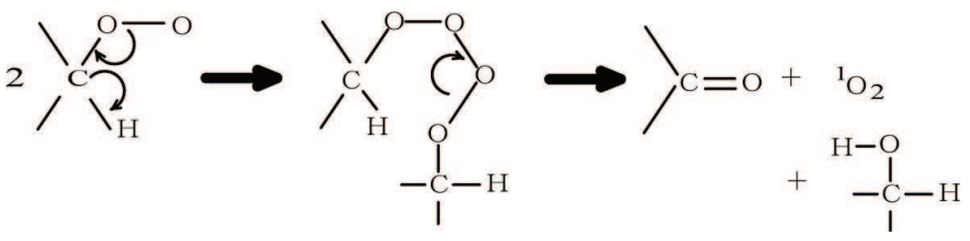

**Figure 9.** The Russell's mechanism [7].

$$ROO \cdot + ROO \cdot \rightarrow R = O + ROH + {}^1O_2 \quad (6)$$

The photo-generation in the visible region has been derived from $^1O_2$ in the past because the lipid peroxidation product is proportion to the emission intensity in the visible region. However, the emission by excited carbonyl involves in Russell's mechanism. Tyrosine and tryptophan emits at the wavelength of 500– 600 nm [7, 8]. A traditional method to detect $^1O_2$-involved chemical technique has no specificity for $^1O_2$ detection. The sensitivity of $^1O_2$ detection in near infrared enables to detect $^1O_2$ specificity because there is no emission material excepted. The heme compounds in the living organism include hemoglobin (blood), myoglobin (muscle), and cytochrome c (mitochondria). These heme compounds play important role in living body. In the case of inflammation in biological membranes, $^1O_2$ is generated by Russell's mechanism. The heme compounds perform catalysis on this occasion. We titrate the generation of $^1O_2$ by adding NaOCl after the excess $H_2O_2$ was put in the reaction chamber. The optical intensity of $^1O_2$ by 13-LOOH with cytochrome c, in $D_2O$ in near infrared was compared with that of a typical $^1O_2$ generating method by mixed NaOCl and $H_2O_2$. The optical yield of $^1O_2$ by 13-LOOH with cytochrome c, in $D_2O$ was decided using a calibration curve. **Figure 10** shows the calibration curve of the $^1O_2$ optical yield at the wavelength of 1.27 μm using the NaOCl-$H_2O_2$ system.

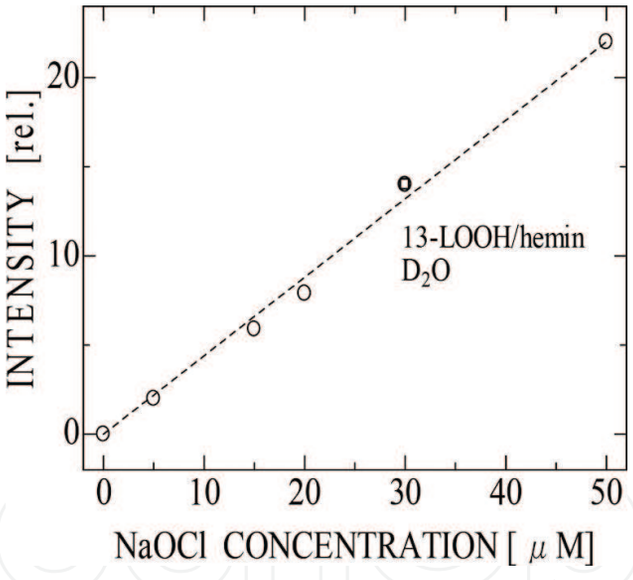


**Figure 10.** Calibration curve of the $^1O_2$ optical yield at the wavelength of 1.27 μm using NaOCl-$H_2O_2$ system.

These results show the degree of risk in case of $^1O_2$ generated from the heme compound. The InGaAs-CIA filter based spectroscopic system will be expected as an analysis equipment of oxidant stress by $^1O_2$.

### 3.2. Multichannel spectroscopic system

The multichannel spectroscopic system is available for measurement of fast emitting phenomena because the optical dispersion device of spectroscopic cannot be avoided to moving for

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wavelength shifting. In the visible region, silicon CCD camera with photoelectron multiplication function for detecting low-level light is commercially available. A silicon multichannel photo device at the wavelength of 1 μm has no photosensitivity. The light detecting materials for the NIR is easily influenced dark current. The commercially available InGaAs CCD or NIR photomultiplier of InGaAs photocathode material is very expensive. Additionally, this system is short of optical sensitivity for $^1O_2$ measurement in the NIR. A highly sensitive 8 channel InGAs-CIA spectroscopic system was developed for $^1O_2$ measurement. A commercially available InGaAs PIN photodiode for an optical communication device was used to stabilize parts supply. In case of employing the high sensitivity multichannel array, each photodiode or Avalanche photo diode device needs a lock-in amplifier with TIA circuits or photon counting equipment. Such a system is difficult to fabricate in reality because it needs many lock-in amplifier or photon counter in proportion to the number of channels. The InGaAs-CIA multichannel system has respectively signal transduction system to voltage from current. The system was allowed simple circuit, signal processing, and signal acquiring system with a low bit AD converter. The outline of InGaAs photodiode array is shown in **Figure 11**. The commercially available photodiode Fujitsu FID13Y13TX has a diameter of 1 mmφ. The 8 photodiodes was fabricated without spacing. The wide size is about 8 mm. Hamamatsu Photonics Co. assembled wire bonding during photodiodes device and packaging.

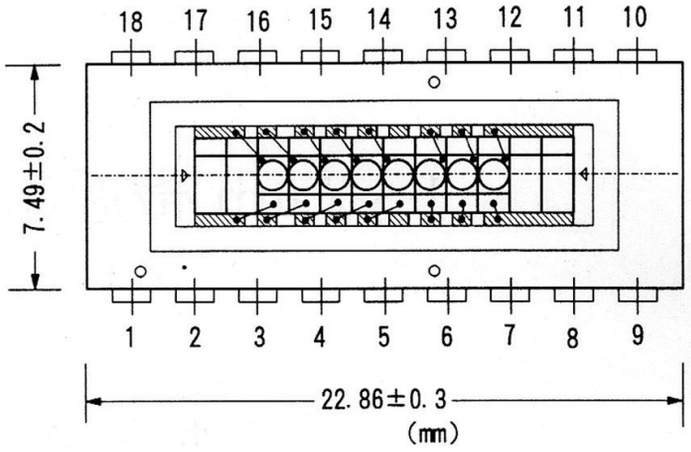


**Figure 11.** Outline of InGaAs photodiode array.

The block diagram of 8 channel multichannel InGaAs-CIA system is shown **Figure 12**. The fundamental circuit is as same as the monocyclic InGaAs-CIA system. The output signal of CIA array was connected to the AD converter for data acquisition after transmitted low impedance by J-FET source follower circuits. The system achieved minimum detectable optical power of $5 \times 10^{-15}$~$10 \times 10^{-15}$. The deviation of sensitivity in each channel was inner single digit.

**Figure 13** shows the block diagram of 8 array InGaAs-CIA multichannel spectroscopic system. The near-infrared light of the optical source was guided to dispersive element after collimator lens for parallel beam through an optical fiber of 100 μm core diameter. The NIR light was dispersed by the grating (Shimazu co. blaze wavelength of 1.2 μm, 300 line/1 mm, efficiency about 60%). The spectroscopic resolution of 1 channel was allowed about 75 nm

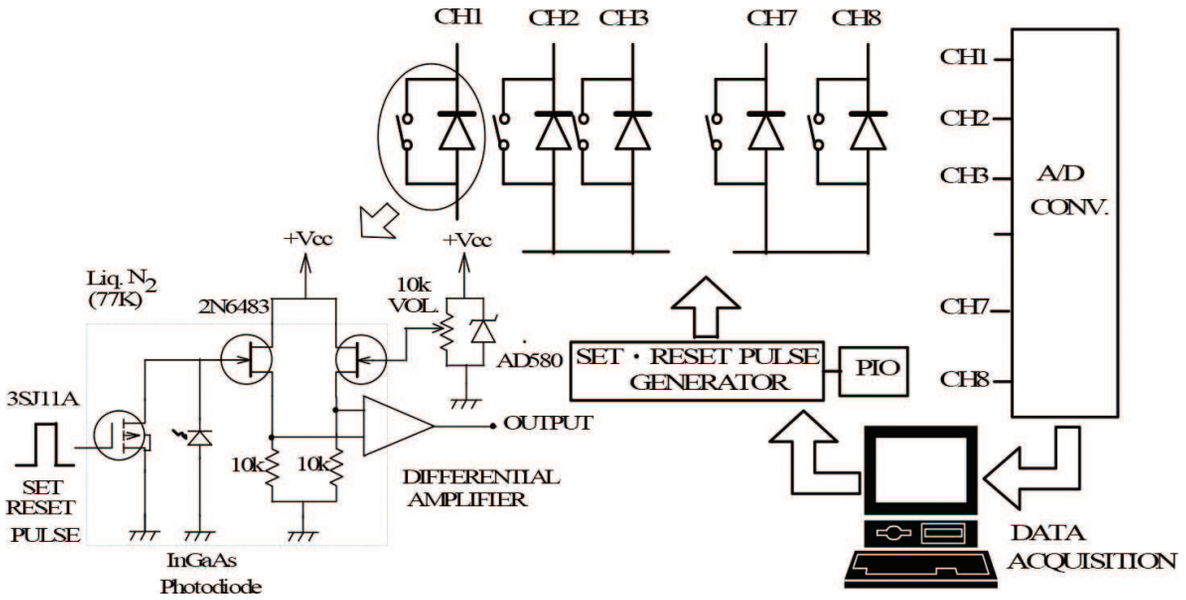


**Figure 12.** 8 multichannel InGaAs-CIA.

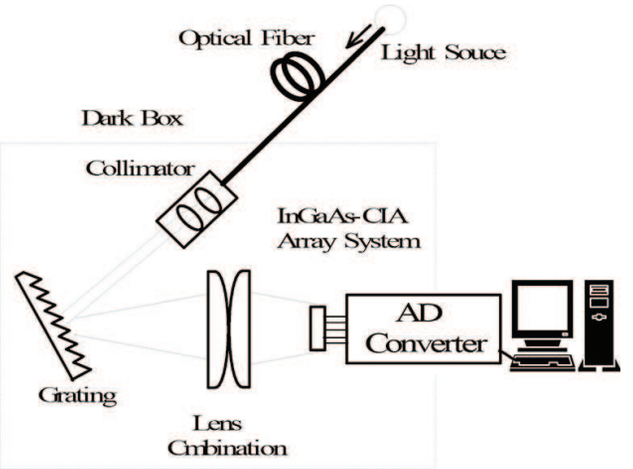


**Figure 13.** 8 array InGaAs-CIA spectroscopic system.

from 1000 to 1600 nm. The dispersion light was condensed on the photodiode array by a focal lens. The calibration of center wavelength on 8 photodiode was achieved using light from the monochromator as an optical band pass filter. The FWHM (full width at half maximum) $^1O_2$ spectrum was broadened about 100 nm at the center of 1265 nm. It needs no detailed resolution for spectrum measurement. In the NIR region, the chemical fluorescence of a biological material has no scarcely existence except $^1O_2$. The low-level light at the center wavelength of 1.27 μm enables to eliminate the thermal background noise.

A proof of any channel of photodiode array was carried out with the wavelength shift by a spectral apparatus of resolution 30 nm of the monochromator from 1000 to 1600 nm. **Figure 14** shows $^1O_2$ spectral of chemiluminescence with NaOCl mixed $H_2O_2$. The spectral of center wavelength was 1.28 μm with 50 nm of full width at half maximum. **Figure 14** shows the spectral of $^1O_2$.

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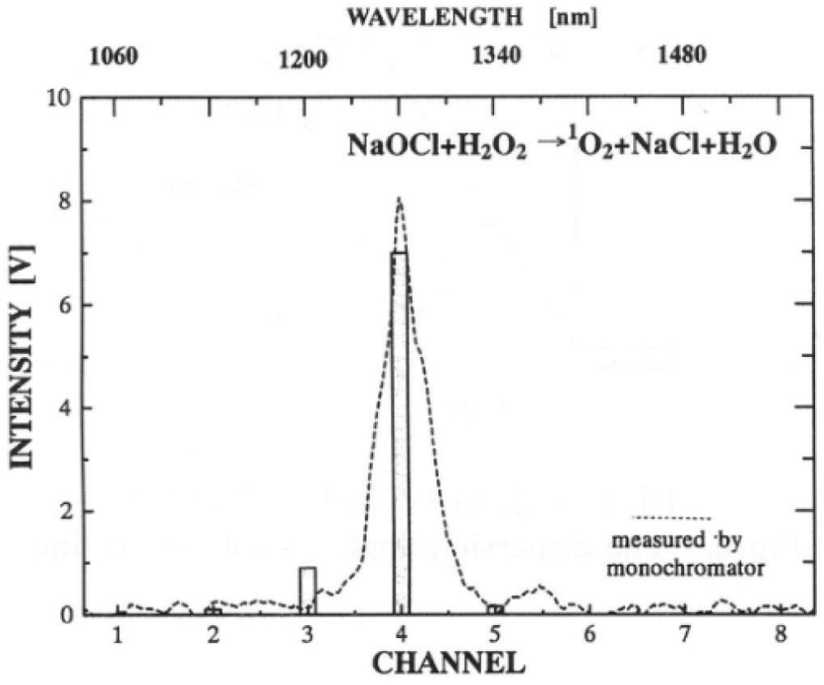


**Figure 14.** $^1O_2$ spectral of chemiluminescence.

The 8 multichannel spectroscopic system succeeded in measurement of $^1O_2$ spectral as same as measurement by the monochromatic spectrometer [9]. The system succeeded in simultaneous multiwavelength of $^1O_2$ spectrum measurement.

This measurement system will be useful for fast optical phenomenon, periodic emission, non-destructive measurement for melon, watermelon, and meat with extremely optical intensity damped in the NIR spectroscopy. The absorption band of protein, sugar, and lipid has a broad spectrum in the NIR. The detection sensitivity and measurement speed are needed. Our multichannel detection system is suitable for such a measurement condition.

### 3.3. $^1O_2$ monitoring system for antioxidant chemical test

In development of antioxidant of food chemistry, found metal material of beauty product, color, the super oxidation power allows the experiments of acid resistance and reaction promotion. In case of acid resistance test, the generation of $^1O_2$ from chemical reaction may influence the chemical generation reaction itself. The generation $^1O_2$ by photoexcited Rose Bengal has almost no influence of chemical reaction. The Rose Bengal $^1O_2$ generation system was fabricated with super luminescence green LED used for the traffic signal. The $^1O_2$ generation intensity was controlled by monitoring NIR chemiluminescence using the InGaAs-CIA system without liquid nitrogen. **Figure 15** shows a block diagram of the $^1O_2$ generation system.

The Rose Bengal solution was photoexcited by the 5W LED of best match absorption band. The new optical excited system achieved the very small compact size in comparison of using argon ion laser. The system is suitable for chemical plants of mass production because the electric power supply circuits for the LED are simple and easy current control. The generated

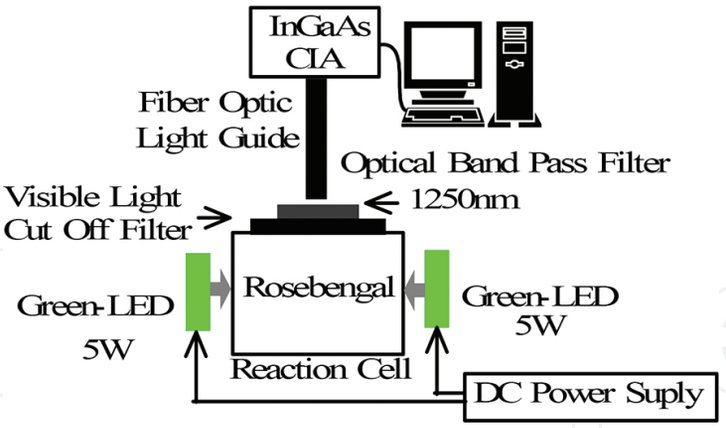


**Figure 15.** Block diagram of $^1O_2$ generation system by use of Rose Bengal.

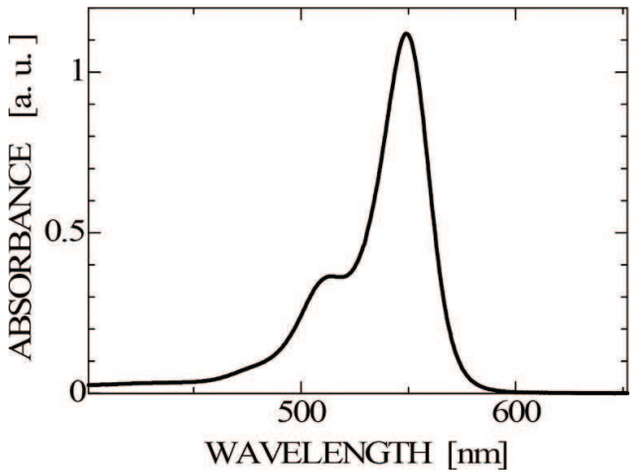


**Figure 16.** Absorption band of Rose Bengal aqueous.

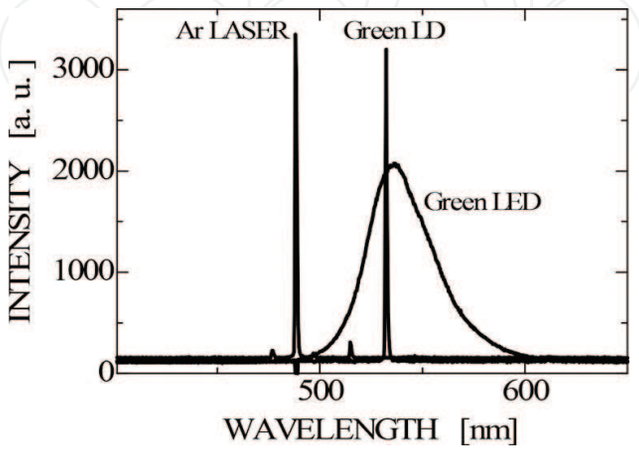


**Figure 17.** Rose Bengal excitation light source.

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$^1O_2$ was optically monitored by InGaAs-CIA at the device temperature of about 150 K degree without liquid nitrogen. The chemical plants should avoid using liquid nitrogen because of choking hazard and troublesome chores. The minimum detectable power of $10^{-13}$ W at the device temperature 150 K was achieved for monitoring $^1O_2$.

The absorption band of Rose Bengal is shown in **Figure 16**. The absorption band covers from 500–600 nm. The absorption peak spectrum yields at the wavelength of 550 nm. The emission spectrum of an excitation light source is shown in **Figure 17**. A water-cooled multimode argon ion laser or green-laser was used for the traditional optical excitation source. The multimode spectrum of argon ion laser is oscillated at the wavelength of 488 and 515 nm. The intensity of spectrum at 488 nm wavelength is stronger than that of 515 nm. The main spectrum stands at the outside of Rose Bengal absorption band. The spectrum of green LED and super luminosity green LED has the center position of the absorption band. The oscillation power of green super luminosity LED for traffic signal has very strong power in comparison with green LD except for metallic processing green LED. The green super luminosity LED permits increasing of absorbance, and achieved downsizing the system spectacularly, and realized cost cuts. **Figure 18** shows photograph of excitation by green LED.

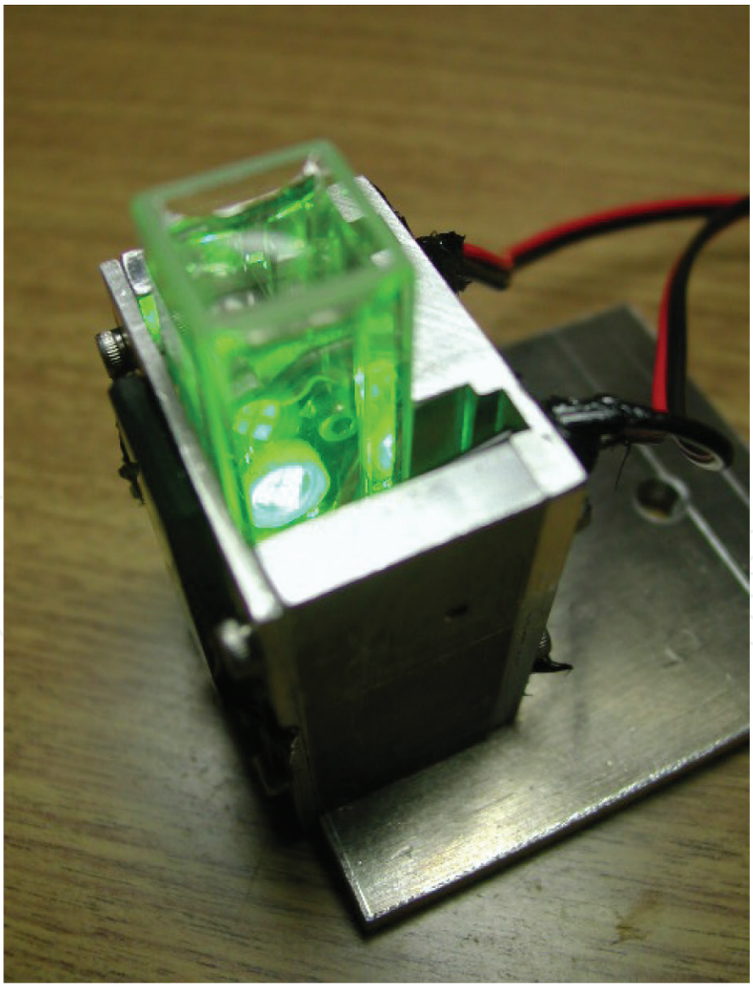

**Figure 18.** Photograph of excitation by green LED.

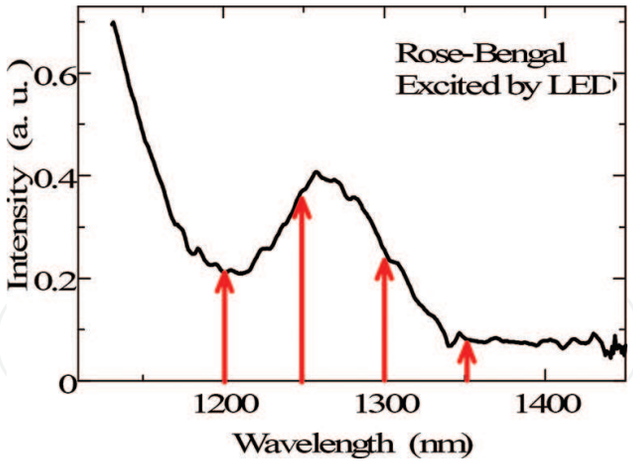


**Figure 19.** $^1O_2$ spectrum of Rose Bengal excited by green LED.

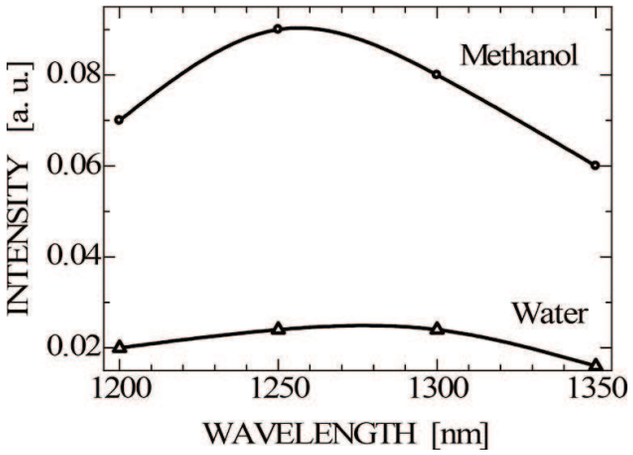


**Figure 20.** $^1O_2$ spectrum of Rose Bengal by measurement with InGaAs-CIA at 150 K.

**Figure 19** shows the spectrum $^1O_2$ of Rose Bengal excited by green LED. The spectrum has a peak at the wavelength of 1.27 μm. A red line in **Figure 19** indicates the wavelength of optical band pass filters. There are four optical band pass filters (1200, 1250, 1300, and 1350 nm) for the spectroscopic system.

The $^1O_2$ emission spectrum of Rose Bengal is shown in **Figure 20**. The intensity of $^1O_2$ emission in methanol is stronger than water solvent. The lifetime of $^1O_2$ in methanol is longer than in water. The generation intensity of $^1O_2$ is monitored through an optical fiber combined with InGaAs-CIA. Many $^1O_2$ monitoring equipment and generation optical sources are necessary in the construction of a microreactor chemical plant. The conventional system employs the Ge-TIA photo detection system with lock-in amplifier and water-cooled argon ion laser. Such a system is not suitable for chemical plant because the system needs occupied large space and high cost. The combination of InGaAs-CIA monitoring and the super luminescence green LED $^1O_2$ generating system enables the construction of a compact and reasonable chemical plant. The system expects to contribute to the development of new medicines.

## 4. Summary

We developed a highly sensitive InGaAs-CIA in the near-infrared region by use of commercially available photodiode. The system performed low-level light detection measurement in the NIR region. The optical emission of $^1O_2$ was detected specifically in the NIR region. The measurement method of $^1O_2$ was changed from the chemical technique to the physical method. We have achieved detection $^1O_2$ of the heme compound in the living organism including hemoglobin (blood), myoglobin (muscle), and cytochrome c (mitochondria) successfully. These heme compounds play an important role in living body, and also generated $^1O_2$ as a catalyst. The InGaAs-CIA system and multichannel detection system for the low-level light was introduced in the NIR region. The system is available for detection of $^1O_2$ from chemical reaction. The electron refrigeration system without liquid nitrogen will be expected to become popular and realize compact size. Especially, we want to make contribution by means of our system to develop the noninvasive photo-sensitive substance for the photodynamic therapy that produces $^1O_2$ caused oxidative damage to the cancer cells.

## Author details

Iwao Mizumoto*, Hiroshi Oguma and Yostumi Yoshi

*Address all correspondence to: mizumoto@nc-toyama.ac.jp

Department of Electronics and Computer Engineering, National Institute of Technology, Toyama College, Toyama, Japan

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