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Optical Sensing of Chlorophyll(in) With Dual-Spectrum Si LEDs in SOI-CMOS Technology

Satadal Dutta[®], Peter G. Steeneken[®], and Gerard J. Verbiest[®]

Abstract—Small and low-cost chlorophyll sensors are popular in agricultural sector and food-quality control. Combining such sensors with silicon CMOS electronics is challenged by the absence of silicon-integrated light-sources. We experimentally achieve optical absorption sensing of chlorophyll based pigments with silicon (Si) micro light-emitting diodes (LED) as light-source, fabricated in a standard SOI-CMOS technology. By driving a Si LED in both forward and avalanche modes of operation, we steer its electroluminescent spectrum between visible (400–900 nm) and near-infrared (~1120 nm). For detection of chlorophyll in solution phase, the dualspectrum light from the LED propagates vertically through glycerol micro-droplets containing sodium copper chloro-



phyllin at varying relative concentrations. The transmitted light is detected via an off-chip Si photodiode. The visible to near-infrared color ratio (COR) of the photocurrent yields the effective absorption coefficient. We introduce the LED-specific molar absorption coefficient as a metric to compute the absolute pigment concentration ($\sim 0.019 \pm 0.006 \text{ mol L}^{-1}$) and validate the results by measurements with a hybrid spectrophotometer. With the same sensor, we also show non-invasive monitoring of chlorophyll in plant leaves. COR sensitivities of $\sim 3.9 \times 10^4 \text{ mol}^{-1}\text{L}$ and $\sim 5.3 \times 10^4 \text{ mol}^{-1}\text{L}$ are obtained for two leaf species, where light from the LED propagates diffusely through the thickness of the leaf prior to detection by the photodiode. Our work demonstrates the feasibility of realizing fully CMOS-integrated optical sensors for biochemical analyses in food sector and plant/human health.

Index Terms—Silicon, avalanche breakdown, CMOS, electroluminescence, optical sensor, light-emitting diode, chlorophyll.

I. INTRODUCTION

C HLOROPHYLL (Chl) is an essential pigment for photosynthesis and a key indicator of health of plants [1]. Moreover, chemically stable derivatives of Chl, e.g. chlorophyllins, are key ingredients in a plethora of dietary and medicinal supplements [2]. Sensors to monitor both natural Chl content in leaves and chlorophyllin in food supplements are, thus, widely used in the agricultural sector and for food-quality control [3]–[5]. Optical sensing is highly suitable to detect Chl and its derivatives. This is due to the strong interaction of

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these pigments with ultraviolet and visible light [6]. While leaf transmittance measurement is popular to monitor Chl noninvasively [7], colorimetric detection of pigments in compact microfluidic systems [8] (and references therein) is becoming popular to ensure fast detection, simple operation and small volume of sample. Advances in semiconductor technology have led to a variety of hybrid light-sources in the same spectral window, e.g. lasers and quasi-monochromatic lightemitting diodes (LEDs), that are employed in the state-of-theart optical sensors [9], [10]. However, these light-sources are incompatible with silicon (Si) CMOS technology, which is the workhorse for advanced electronic read-out and data processing modules for sensors [11]. This hinders device integration and makes these sensors relatively expensive and bulky.

Silicon photonics is emerging as a key technology for the development of CMOS-integrated optical devices for applications in bio-chemical sensing and data communication links [12]–[19]. Interestingly, Si p-n junction diodes exhibit broad-spectrum electroluminescence (EL) at wavelengths (λ) near 1120 nm in forward mode (FM) and at λ in the range of 400–900 nm in avalanche mode (AM) operation.

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Fig. 1. Schematic block diagram illustrating the optical sensing method. Optical coupling from the Si LED on the CMOS chip to an externally mounted Si PD (reverse biased at 1 V) is measured in presence of a pigmented glycerol droplet (top panel) or a leaf (bottom panel) on top of the LED. The LED is operated in (a) forward mode (FM) and (b) avalanche mode (AM). The pigment (NaCuChI) absorbs light in the range 400 < λ < 800 nm. (c) Schematic of the measurement set-up (not to scale). The on-chip LED is placed on a vacuum chuck and is driven in constant current mode, where electrical probing is done via aluminium bond-pads and tungsten needles. The wavy arrows indicate light propagation.

Although this EL occurs at a low quantum efficiency $(\sim 10^{-3} - 10^{-5})$ [20]–[26] due to the indirect bandgap of Si, for many applications the advantages of CMOS integration of the LED outweigh the drawback of low efficiency. Recent advancements [27]-[29] have successfully highlighted the Si LED as a promising candidate for monolithically integrated optical interconnects due to the high responsivity of Si photodiodes (PDs) for wavelengths (λ) < 1000 nm. The ability to electrically switch between visible (VIS) and near-infrared (NIR) emission from a single Si LED eliminates the need for any process modification or device replacement in an optical sensor. In contrast, wavelength tuning in LEDs made of III-V semiconductors require large stoichiometric changes in material composition [30]. The 400 – 1300 nm spectral range is highly suitable for sensing photosynthetic pigments [6], leaf-water status [33], [34], colored contaminants in water [35]–[37] and blood oxygen levels [38].

In this work, we show how Si LEDs fabricated in a standard SOI-CMOS technology are viable light-sources for use in optical absorption sensing systems, by driving a single LED in both FM and AM operation. The emitted light propagates vertically through a pigmented micro-droplet placed on the surface followed by detection by a discrete Si PD mounted externally above the chip (see Fig. 1(a), (b)). We define the color ratio (COR) as ratio of PD photocurrent during AM LED operation to that during FM LED operation. From the COR and the mean height of the droplet (optical path length), we obtain the effective absorption coefficient (α) of the pigmented solution specific to our broadband Si LED. In our recent conference proceedings paper [31], we demonstrated this sensing principle using Carmine pigment. In this paper, we extend our work by sensing Chl-based pigments, namely sodium copper chlorophyllin (NaCuChl) in solution phase and chlorophyll (Chl) in intact plant-leaves.



Fig. 2. (a) Top-view micrograph and (b) device cross-section of the n⁺p junction LED in a SOI-CMOS technology from NXP Semiconductors [32]. Symbols A and K indicate the anode and cathode terminating in Al bond pads. The LED has a junction area of 45 \times 45 μ m², and a reverse breakdown voltage of ~17 V.

The rest of the manuscript is organised as follows. Section II describes the experimental device and the method. Sections III-B and III-C present the measurement results and data analyses for sensing with droplets (containing NaCuChl in solution) and with intact leaves (containing naturally occurring Chl.), respectively. Section IV briefly outlines the merits, applicability and future scope of the sensor. Section V summarizes our work.

II. EXPERIMENTAL SET-UP AND METHOD

Fig. 1(c) shows a schematic diagram of the set-up. The on-chip Si LED is placed on a vacuum chuck. The bondpads are electrically probed by Tungsten needles connected to EverBeing EB-050 micropositioners in a probe station. A BPW34 Si PD from Vishay semiconductors is mounted above the chip at a center-height \sim 5 mm tilted at \sim 45 degrees via a micropositioner. The LED is driven in a constant current (sweep) mode and the PD is driven at a fixed reverse bias of 1 V using a Keysight B2912A precision source and measurement unit (SMU). During measurement, either a droplet with NaCuChl. or a leaf is placed on top of the Si LED.

Figs. 2(a) and (b) show, respectively, the optical top-view micrograph (layout), and the schematic device cross-section of the test LED, designed in a standard 130 nm silicon-on-insulator (SOI) CMOS technology [32], from NXP Semi-conductors. The LED is a vertical n⁺p junction diode with a junction depth of ~0.25 μ m, an active junction area of 45 × 45 μ m², and an avalanche breakdown voltage of ~17 V [27]. Vertical poly-Si columns are placed near the p-n junction, which connect the SOI layer to the Si substrate. They serve as heat sinks to reduce the thermal resistance significantly.

In a first experiment, we test the sensing principle using droplets containing NaCuChl. A commercially available solution (~10 mM) of NaCuChl (E141), from PipingRock Health Products, LLC. is used as a target. We choose glycerol as the solvent for the droplets. This choice is motivated by its negligible volatility at 300 K, optical transparency for λ in the range 400–1200 nm, and chemical inertness to the SiO₂ layer on the chip surface. We denote the NaCuChl. concentration of the target solution as c_{ref} . This solution is diluted in appropriate volumes of excess glycerol to yield solution specimens of the following relative concentrations (c/c_{ref}) of C1 = 1.0 %,



Fig. 3. (a) Solution specimens of sodium copper chlorophyllin (NaCuChI) diluted in laboratory-grade glycerol with indicated concentrations (% by volume) relative to a reference commercial solution (\sim 10 mM) of NaCuChI (E141) in glycerol and water. C0 represents only glycerol. (b) Method for ChI. monitoring in leaves. To emulate chlorophyll deficiency, the test leaf is treated with 12 mL ethanol at 300 K in a graduated vial. At every 2 hour interval, optical transmission through the leaf is measured with the sensor and the absorbance of the ethanol extract is measured with the spectrophotometer set-up as illustrated in (c). A fiber-coupled AvaLight-DH-S-BAL light-source (Deuterium and halogen) shines a collimated beam through the solution (C1) in a UV-cuvette with 1 cm optical path. The transmitted beam is fed to an AvaSpec-ULS2048CL-EVO spectrometer (200–1100 nm) via a multimode 400 μ m core optical fiber.

C2 = 2.5 %, C3 = 6.25 %, C4 = 12.5 %, and C5 = 25.0 %, as shown in Fig. 3(a). We label our solvent as C0 (c=0). The PD photocurrent ΔI_{PD} (Δ represents that the dark current has been subtracted) is measured in air and in presence of a microdroplet, which is transferred from each solution specimen with a hydrophilic tip of a ~100 μ m core silica fiber. The dropletson-chip have lateral diameters >500 μ m, and hence covers the on-chip LED entirely (Fig. 1(c)), as was shown in our earlier work [31]. The same droplet is used to measure ΔI_{PD} by driving the same LED in AM and FM operation at bias currents $I_{LED} = 1-6$ mA.

In the second experiment, we collect fresh green leaf specimens, one each from Hamamelis virginiana L. and Capsicum annuum L. plants. The leaves are then washed with demi water and wiped dry to remove dust and impurities from the surface. The PD photocurrent is then measured with the setup described above, with the adaxial surface of the fresh leaf facing the on-chip LED (Fig. 1(c)). Each leaf is inserted into a vial containing 12 mL of ethanol at 300 K. The ethanol treatment emulates Chl stress in the leaf as the photosynthetic pigments dissolve in ethanol. After time t = 2, 4, 6, 8, and 10 hours, the leaf is withdrawn from its vial (Fig. 3(b)) and the corresponding PD photocurrent is measured. At each timestamp, the ethanolic extract is also sampled to measure its spectral absorbance with a hybrid spectrophotometer set-up illustrated in Fig. 3(c). This set-up consists of a fiber-coupled AvaLight-DH-S-BAL light source (Deuterium plus halogen) that shines a collimated beam through a UV-cuvette containing the test solution with 1 cm optical path. The transmitted beam is fed to an AvaSpec-ULS2048CL-EVO spectrometer (200–1100 nm) via a multi-mode 400 μ m core optical fiber.



Fig. 4. Avalanche-mode (400–900 nm) and forward-mode (1000–1270 nm) normalized electroluminescent intensity spectra of the Si LED (in black) measured with a ADC-1000-USB and AvaSpec-UV/ VIS/NIR spectrometers respectively from Avantes B.V. The measured molar absorption coefficient spectrum (in green) of NaCuChl in glycerol is measured with the hybrid spectrophotometer set-up shown in Fig. 3(c), and calibrating the value at $\lambda = 626$ nm from [2].

III. RESULTS AND ANALYSIS A. LED EL-Spectra and NaCuChl Molar Absorption Coefficient

Light emission from forward-biased Si diodes at λ in the range 1000–1270 nm, results from indirect (phononassisted) recombination of electron-hole pairs near the bandedge [20]. When the diode is reverse biased above the avalanche breakdown voltage, the high electric field in the depletion region accelerates the charge carriers to energies exceeding the bandgap of 1.12 eV. This leads to high-energy inter-band electronic transitions, resulting in a broad-spectrum EL peaking in the 600–700 nm wavelength window [22], [23], [25]. Fig. 4 shows the normalized EL spectra of the n⁺p junction LED [27], [31] measured in avalanche-mode (AM) and forward-mode (FM) operation, with a UV/VIS (ADC-1000-USB) and AvaSpec-NIR spectrometer from Avantes B.V., respectively. The power normalized EL spectral irradiance $\varepsilon(\lambda)$ [nm⁻¹]is defined by:

$$\varepsilon(\lambda) = \frac{E(\lambda)}{\int_{\lambda} E(\lambda) \cdot d\lambda},\tag{1}$$

where $E(\lambda)$ is the measured EL intensity, and integration limits are from $\lambda = 400$ nm till $\lambda = 900$ nm. The AM EL spectrum has a significant overlap with the absorption spectrum of NaCuChl, whereas the same chemical absorbs negligibly in the FM EL spectrum of the Si LED. Fig. 4 also shows the molar absorption coefficient $\alpha_{\rm M}(\lambda)$ of our NaCuChl solution in glycerol. The specimen C1 $(c_1/c_{\rm ref} = 0.01)$ is used for this purpose and the absorbance $A(\lambda)$ is measured with the spectrophotometer set-up. The absorption coefficient of the specimen C1, $\alpha_{\rm C1}(\lambda)$ [cm⁻¹] is calculated from Beer-Lambert's law as:

$$\alpha_{\rm C1}(\lambda) = -\frac{\ln(1 - A_{\rm C1}(\lambda))}{L_{\rm opt}},\tag{2}$$



Fig. 5. Photocurrent (at reverse bias of 1 V) in the Si PD versus LED current in avalanche (-X axis) and forward (+X axis) modes of operation in air (squares), in presence of glycerol droplets from specimens C0 (white circles), C1 (green circles) and C2 (green diamonds). (Inset): Schematic cross-section showing the light-rays being focused by the plano-convex micro-lens formed by the droplet.

where $L_{opt} = 1$ cm is the optical path length of the light beam in the cuvette (see Fig. 3(c)). Subsequently, $\alpha_{\rm M}(\lambda)$ [cm⁻¹mol⁻¹L] is estimated as:

$$\alpha_{\rm M}(\lambda) = \left(\frac{c_{\rm ref}}{c_1}\right) \cdot \left(\frac{\alpha_{\rm C1}(\lambda)}{\alpha_{\rm C1}(626\rm{nm})}\right) \cdot 7192 \tag{3}$$

where we have used the literature reported molar absorption coefficient of NaCuChl as 7192 cm⁻¹mol⁻¹L at $\lambda = 626$ nm (Q-band) [2] as a calibration point.

In order to use the Si LED as the light source for optical transmission measurements, we first compute the LED-specific molar absorption coefficient $\alpha_{\rm M}^{\rm LED}$ [cm⁻¹mol⁻¹L], and is expressed as:

$$\alpha_{\rm M}^{\rm LED} = \int_{\lambda} \alpha_{\rm M}(\lambda) \cdot \varepsilon(\lambda) \cdot d\lambda, \qquad (4)$$

where the limits of integration are the same as in eq. (1). We obtain $\alpha_{\rm M}^{\rm LED} = 4782.7 \text{ cm}^{-1} \text{mol}^{-1} \text{L}$. Note that $\alpha_{\rm M}^{\rm LED}$ is a quantitative way to express the overlap between the $\varepsilon(\lambda)$ and $\alpha_{\rm M}(\lambda)$ (indicated by the shaded region in Fig. 4).

B. Sodium Copper Chlorophyllin in Glycerol-Droplet

Fig. 5 shows the measured PD photocurrent (at a reverse bias of 1 V) which varies linearly with I_{LED} in both AM and FM LED operation, showing a linear relationship between optical power and I_{LED} . We observe that $\Delta I_{\text{PD}}^{\text{AM}} > \Delta I_{\text{PD}}^{\text{FM}}$ at any given I_{LED} . This is primarily due to the higher PD quantum efficiency for light emitted in AM operation [27]. Further, we observe that both $\Delta I_{\text{PD}}^{\text{AM}}$ and $\Delta I_{\text{PD}}^{\text{FM}}$ are, respectively, a factor of ~3.2 and ~2.0 higher in presence of the glycerol droplet (CO) as compared to transmission in air. This is explained by two factors. Firstly, there is a good refractive index matching between glycerol (n \approx 1.47) and SiO₂ (n \approx 1.45) over the droplet-covered die area. Secondly, the droplet acts as a plano-convex lens leading to a gain in the optical extraction efficiency (see inset of Fig. 5). A mismatch in the optical extraction efficiency between AM and FM operation is likely due to possible electrostatic effects on the shape or on the refractive index [39] of the glycerol droplet at widely different values of LED bias voltages: \sim 19 V for AM and \sim 1 V for FM LED. Since the pigment absorption window overlaps only with the AM EL spectrum, we can express the photocurrent in presence of the droplet for FM and AM LED operation, respectively as

$$\Delta I_{\text{PD}(\text{Gly})}^{\text{FM}}(c_i) = \eta_{\text{LED}}^{\text{FM}} \cdot \eta_{\text{PD}}^{\text{FM}} \cdot \eta_{\text{Gly}}^{\text{FM}} \cdot I_{\text{LED}}$$
(5)
$$\Delta I_{\text{PD}(\text{Gly})}^{\text{AM}}(c_i) = \eta_{\text{LED}}^{\text{AM}} \cdot \eta_{\text{PD}}^{\text{AM}} \cdot \eta_{\text{Gly}}^{\text{AM}} \cdot I_{\text{LED}} \cdot \exp[-\alpha(c_i) \cdot h]$$
(6)

where *h* is the droplet height, and c_i represents the concentration of the *i*th solution (*i*=0, 1, 2, 3, 4, 5). Here η_{LED} and η_{PD} represent the external quantum efficiencies of light-emission from the LED and light-detection by the PD, respectively. η_{Gly} is the light-extraction efficiency from the chip through the droplet. Considering a measurement error of ± 2 pA in the photocurrent, we observe in Fig. 5 that for droplets containing NaCuChl., absorption of visible light by the pigment leads to a decrease in $\Delta I_{\text{PD}}^{\text{AM}}$, as compared to transmission via the pure glycerol droplet. Small discrepancies in $\Delta I_{\text{PD}}^{\text{FM}}$ among droplet specimens are likely due to uncertainties in the droplet height and coverage area of the droplet, as was also observed in our earlier work [31].

Dividing eq. (6) by (5), we obtain the color ratio (COR) of optical coupling in AM to FM as:

$$\operatorname{COR}(c_i) = \left(\frac{\Delta I_{\text{PD}(\text{Gly})}^{\text{AM}}(c_i)}{\Delta I_{\text{PD}(\text{Gly})}^{\text{FM}}(c_i)}\right)$$
$$= \left(\frac{\Delta I_{\text{PD}(\text{Gly})}^{\text{AM}}(c_0)}{\Delta I_{\text{PD}(\text{Gly})}^{\text{FM}}(c_0)}\right) \cdot \exp[-\alpha(c_i) \cdot h]$$
$$= \operatorname{COR}(c_0) \cdot \exp[-\alpha(c_i) \cdot h]$$
(7)

where $\alpha(c_i) = \alpha_{\rm M}^{\rm LED} \cdot c_i$ is the effective absorption coefficient of the solution *Ci* from which the droplet is sampled, and c_0 represents pure glycerol (hence, $\alpha = 0$). Fig. 6 shows the measured COR versus relative concentration $c/c_{\rm ref}$. The values are averaged over the set with $I_{\rm LED} = [1, 2, 3, 4, 5, 6]$ mA. We observe that COR decreases with increasing c in accordance with Beer-Lambert law ($\propto \exp[-\alpha \cdot h]$). An exponential fit (least-squares method) yields the attenuation constant $\beta = 1.495$. Thus, we obtain the concentration of the target solution $c_{\rm ref}$ as

$$c_{\rm ref} = \frac{\beta}{h \cdot a_{\rm M}^{\rm LED}} \tag{8}$$

The droplet height *h* is estimated from optical microscopy as shown in Fig. 7(a). For droplets of size ranging from ~100 μ m - ~1 mm, *h* is primarily governed by the angle of contact [40], [41] at the local liquid-chip (SiO₂) interface and the surface tension. Both parameters have uncertainties due to local surface properties and impurities (including the pigment) in the solvent. This results in a statistical variation in *h*, which is captured in Fig. 7(b) by analyzing multiple glycerol



Fig. 6. Color ratio (AM to FM operation of the Si CMOS LED) of the PD photocurrent when light transmission occurs through the microdroplets sampled from solution specimens C0 to C5. The values for COR are averaged over $l_{\text{LED}} = 1-6$ mA. COR decreases exponentially with increasing *c* (black solid line). The fitted attenuation constant $\beta = (\alpha_{\text{ref}}^{\text{LED}} \cdot h)$ is a function of the effective absorption coefficient of the reference NaCuChl. solution, and the droplet height *h* (see inset).



Fig. 7. (a) Optical micrograph of the side-view of a droplet-on-chip sampled from solution C3 showing the height profile. The estimated volume of the droplet was ~0.1 μ L. (b) Histogram showing the mean and standard deviation in the measured center-height of different droplets transferred to the chip with a silica fiber tip. (c) Estimated concentration of the target NaCuChl solution (c_{ref}) via the Si LED based sensor (green) and via the hybrid spectrophotometer (black). The standard error of the Gaussian curves represents the uncertainty in experiment, while the mean represents the estimated value.

droplets on multiple dies. We observe $h = 164.50 \pm 50.24 \,\mu$ m, where the error represents the standard deviation under a uni-modal Gaussian fit. Hence, using eq. (8) we obtain $c_{\rm ref} = 19.0 \pm 5.8 \,\,{\rm mmol.L^{-1}}$ (mM). Fig. 7(c) shows this result graphically with a Gaussian likelihood curve, where the error in our estimation is represented by the standard deviation (σ).



Fig. 8. Estimated concentrations of the diluted NaCuChl solution specimens C1–C5 via the Si LED based sensor, represented by a Gaussian likelihood curve. The standard error of the Gaussian curves represents the uncertainty in experiment, while the mean represents the estimated value.

We validate the estimated c_{ref} , by an independent absorbance measurement on the specimen C1, using the hybrid spectrophotometer (SP) set-up as:

$$c_{\rm ref}^{\rm SP} = \left(\frac{\alpha_{\rm C1}(626\rm{nm})}{\alpha_{\rm M}(626\rm{nm})}\right) \cdot \left(\frac{c_{\rm ref}}{c_1}\right) \tag{9}$$

where $\alpha_{C1}(626nm)$ is obtained from eq. (2). This gives $c_{ref}^{sp} = 13.3 \pm 0.7 \text{ mmol.L}^{-1}$ (mM), which is in a close agreement with that obtained by our droplet sensing method with the broad-band Si LED. A small positive deviation in the estimated value with our sensor is likely due to an underestimation of α_{M}^{LED} , where we have ignored the contribution of the weak absorption tail of NaCuChl for $\lambda > 900$ nm in eq. (4). Error could also arise due to possible inhomogeneities in the diluted specimens (high viscosity of glycerol).

For specimens C1 to C5, the concentrations can also be obtained independently using eq. (7) as

$$c_i = \left(\frac{1}{h \cdot \alpha_{\rm M}^{\rm LED}}\right) \cdot \left(-\ln\left[\frac{\rm COR(c_i)}{\rm COR(c_0)}\right]\right) \tag{10}$$

which yields $c_1 = 0.5\pm0.2$ mM, $c_2 = 2.1\pm0.6$ mM, $c_3 = 3.0\pm0.9$ mM, $c_4 = 3.5\pm1.1$ mM, and $c_5 = 4.9\pm1.5$ mM, as shown graphically in Fig. 8. Note that the standard error in the estimations propagates predominantly from the error in *h*. Taking the 1st order derivative approximation of eq. (10), we get $\delta c_i = c_i \cdot (\delta h/h)$. Consequently, the absolute error is proportional to the concentration c_i . In order to evaluate the sensitivity $S_{droplet}$ of our sensor, we apply the differential approximation to eq. (7) that gives us

$$S_{\text{droplet}} = \frac{\delta \text{COR}(c_i)}{\delta c_i} = -\text{COR}(c_i) \cdot \alpha_{\text{M}}^{\text{LED}} \cdot h \qquad (11)$$

where the minus sign indicates that COR decreases with increasing c. At low concentrations, e.g. for specimen C1, we obtain $|S_{droplet}| = 330 \text{ mol}^{-1}\text{L}$.

C. Non-Invasive Sensing of Chl. Deficiency in Leaves

Chlorophyll (Chl. a,b) and carotenoids (β -carotene) are the two naturally occurring dominant photosynthetic pigments [6],





Fig. 9. Measured spectral absorbance of ethanolic solutions of photosynthetic pigments extracted from *Hamamelis* and *Capsicum* leaf samples, treated with 12 mL ethanol for 2 hours at 300 K. The peak at $\lambda \approx 660$ nm is a signature of Chl. a, while the local peak at $\lambda \approx 475$ nm indicates the presence of carotenoids. (Inset): Hybrid spectrophotometer set-up used for the absorbance measurement.

crucial for the growth and nutrition in plants. Reduction of Chl in leaves (chlorosis) is an important marker of plant stress. The measured absorbance (A) spectra of pigments extracted (in ethanol) from leaves of two example species, namely Capsicum annuum L. and Hamamelis virginiana L., are shown in Fig. 9. The ethanolic extracts were sampled after a duration of 2 hours of dissolution at 300 K, and analyzed with the hybrid spectrophotometer set-up (see inset). Both spectra exhibit peaks at $\lambda_{\rm R} \approx 660$ nm, $\lambda_{\rm B} \approx 475$ nm, and $\lambda_{\rm V} \approx 430$ nm. The peaks at $\lambda_{\rm R}$ and $\lambda_{\rm V}$ are attributed to Chl. a, and the peak at $\lambda_{\rm B}$ is a signature of β -carotene [6], where small deviations (± 5 nm) [42] in peak positions may occur due to different solvents used. We observe that the AM EL spectrum of the Si LED has a maximum overlap with the absorption of Chl. a, followed by a relatively smaller overlap with that of carotene.

The COR was measured for the Capsicum and Hamamelis leaves at different timestamps of ethanol treatment. This was done by placing the leaves on top of the Si CMOS LED in our sensor and measuring light transmission through the leaf. The COR in the PD photocurrent against the measured absorbance of the corresponding ethanolic extract sampled immediately after withdrawing the Capsicum and Hamamelis leaf from the vial, are shown in Fig. 10(a) and (b), respectively. Also shown in the same figure are the corresponding Chl. a concentrations (c) (in solution) calculated from measured A(660 nm) and the literature-reported [43]-[45] $\alpha_{M(ChlA)}(660 \text{ nm})$ of 32640 cm⁻¹mol⁻¹L. We observe a linear relationship (high correlation) between the COR and A. This is expected because the total amount of pigment molecules is conserved during the physical dissolution process. Hence, as the optical transmission through the leaf increases, the [Chl. a] in solution increases. The slope of the linear fit gives us $\delta COR/\delta A[\%] = 0.024$ and 0.0325 for *Capsicum*



Fig. 10. COR (for the leaf) versus 660 nm absorbance (in ethanolic solution) for (a) *Capsicum* and (b) *Hamamelis* leaf samples with indicated error bars (symbols). The COR was measured by placing the leaf on the Si CMOS LED (see inset). The black solid line represents the linear fit, with a slope representing the mean sensitivity (δ COR/ δ A[%]). The top X-axis maps the absorbance to the equivalent Chl. a concentration by using $\alpha_{M(Ch|A)}(660 \text{ nm}) = 32640 \text{ cm}^{-1} \text{ mol}^{-1} \text{L}.$

and *Hamamelis* respectively. Considering an error margin of ± 0.2 in the COR (measured through the leaf), we obtain a resolution (and hence the detection limit) of absorbance $\delta A_{\text{res}}[\%]$ of $\approx 8.3 \%$ and $\approx 6.2 \%$ for the *Capsicum* and *Hamamelis* leaf respectively. Further, using a differential approximation of eq. (2), we can calculate the detection limit in terms of concentration (in solution) *c* as:

$$\delta c_{\rm res} = \left(\frac{1}{\alpha_{\rm M(ChlA)} \cdot L_{\rm opt}}\right) \cdot \left(\frac{\delta A_{\rm res}}{100 - A[\%]}\right)$$
(12)

Thus, we obtain $\delta c_{\text{res}} \approx 5 \ \mu\text{M}$ for *Capsicum* and $\approx 3.8 \ \mu\text{M}$ for *Hamamelis* respectively, for a reference value of A = 50% (in solution), and $L_{\text{opt}} = 1$ cm (path length in cuvette).

Further we can define the mean sensitivity (S_{leaf}) of our sensor as

$$S_{\text{leaf}} = \frac{\delta \text{COR}}{\delta(c_{\text{ChlA}})} = \frac{\delta \text{COR}}{\delta A[\%]} \cdot \frac{\delta A[\%]}{\delta(c_{\text{ChlA}})}$$
$$= \left(\frac{\delta \text{COR}}{\delta A[\%]}\right) \cdot \alpha_{\text{M(ChlA)}} \cdot L_{\text{opt}} \cdot (100 - A[\%]) \quad (13)$$

where A is obtained by rearranging eq. (2) as $100 \times [1 - \exp(-\alpha_{M(ChlA)} \cdot L_{opt} \cdot \Delta n_{ChlA}/V_{sol})]$. S depends on Δn_{ChlA} . Substituting values, we obtain $S_{leaf} = 3.9 \times 10^4 \text{ mol}^{-1}\text{L}$ and $5.3 \times 10^4 \text{ mol}^{-1}\text{L}$ for the *Capsicum* and the *Hamamelis* leaf, respectively, for a reference A = 50%. Differences in S between the two leaf species obtained by this method is due to sample-to-sample variation. This can be attributed to the different optical paths through the different cellular arrangements in the inner mesophyll tissue of the two leaves, and the different spatial distribution of Chl.

IV. DISCUSSION AND OUTLOOK

We have presented the first proof-of-concept small-volume (~0.1 μ L) optical absorption sensor with broad-spectrum avalanche-mode Si LEDs in standard CMOS technology. The same LED emits light with two disjoint and bias-dependent EL-spectra, only one of which is absorbed by a target specimen. This obviates the need for modifications in fabrication process and material composition, which are typically employed in tailoring the efficiency and EL-wavelength of Si-based light sources, as summarized in Table I. We outline the performance, future scope and applicability of our sensor under the following headings:

A. Resolution and Sensitivity

In solution phase, the dominant source of error in c_{ref} in our experiment is the uncertainty in h, and thus, not limited by the LED or PD. For specimen C1 (the lowest concentration), we obtain a resolution of ~200 μ M (Fig. 8). If the droplet height is known precisely, then the error in our experiment will be dominated by the 4 % relative uncertainty in measuring COR(c_i). Using eq. (10), we then obtain that $\delta c_1/c_1$ to be ~8 %. This amounts to an absolute error of 40 μ M. Increasing the precision of the dispensed volume of the micro-droplet is envisaged in future developments, which will reduce the error and hence increase the resolution towards state-of-the-art (~1 μ M) [46], [47] that uses hybrid quasimonochromatic LEDs with III-V semiconductors in relatively bulky sensors.

Eqs. (11) indicates that at a given reference concentration, sensitivity is proportional to the optical path length through which absorption takes place. In the non-invasive detection via a leaf, we emulate Chl stress by systematic reduction in the photosynthetic pigments via the ethanol treatment. The inner micro-structure of a leaf is largely a matrix of loosely packed mesophyll cells with a certain fraction of inter-cellular voids [48]. Light from the Si LED propagates through these mesophyll cells in a diffuse manner (multiple Fresnel reflections at the cell-void interfaces) [49], [50] before emerging into air and being collected by the photodiode. The light from the LED is divergent and hence it illuminates a patch of area $\sim 10 \text{ cm}^2$ on the leaf. The color ratio measured is therefore averaged out over this spot, which relaxes the constraints on precise alignment. Thus, the net optical path is folded by a large leaf-dependent factor. Hence, detection with the intact leaf is expected to yield a higher sensitivity, as compared to the measurement in solution. The only trade-off in using a leaf directly is the inclusion of local variations in pigment distribution and optical path length through the leaf tissue in a single leaf.

B. Stability

Glycerol, being a low-voltatile (boiling points > 400 K) [51], polar and organic solvent, is a suitable choice for the medium to dispense stable micro-droplets. The back-end oxide layer in the CMOS chip provides good passivation to shield the Si LED from chemicals in the droplet. Postremoval of droplet with iso-propanol, the chip surface was re-used for the next droplet with negligible change in ΔI_{PD} . However, only the Al-capped bond pads limit the degree of re-usability of the sensor in solution-phase due to possible (electro-)chemical side-reactions with and glycerol [52], [53] and water. For sensing carmine [31], the same device could be re-used for upto 6 droplet specimens, while for NaCuChl upto 3 droplets could be measured, before the Al-capping was corroded. For a given droplet, the measurements shown in Fig. 5 were stable for at least \sim 5-7 minutes. Longer duration of LED operation resulted in reactions between the Al-capped bond pads and glycerol, which in turn affects the shape of the droplet and pigment homogeneity.

C. Device Footprint and Power Consumption

With the exception of the off-chip Si PD, our sensor has a footprint of less than $\sim 0.5 \text{ mm}^2$, which includes a dualspectrum light-source within an area of $\sim 0.01 \text{ mm}^2$. For industrial CMOS technologies, the production costs for silicon are typically 10-50 eurocents per mm² of die area. So, the cost of a single Si LED is estimated to be within a eurocent. Monolithic integration of the Si PD with a dedicated layout will further reduce the form factor of the sensor, which will be studied in our future work. From the viewpoint of fieldimplementation of such a sensor, either open-cavity or glass-lid packaging would be preferred. In the latter scenario, an additional \sim 7 % loss in optical power is expected due to reflections at the air-glass interfaces. The dc power consumption in our LED ranged from 18 mW ($I_{LED} = 1$ mA) till 118 mW $(I_{\text{LED}} = 6 \text{ mA})$. For each I_{LED} , an integration time of ~500 ms was used to reduce the noise in measuring the corresponding photocurrent with the SMU, leading to a minimum energy consumption of 10 mJ. In a prior work, the thermal resistance on the chip at a distance of 10 μ m from the LED was extracted to be 35 K/W [27]. Thus, for an electrical input power of 20 mW, the increase in steady-state temperature due to selfheating in the LED is within 1 K. The CMOS technology is widely successful to provide high-level monolithic integration

Light-emitter type	Typical EL	Optical power efficiency	Standard CMOS	Wavelength	References
type	wavelength [nm]	[order of magnitude]	compatibility	selection	
c-Si p-n junction	400-900 (avalanche)	$10^{-3} - 10^{-6}$	Yes	By switching	[19], [20],
(this work)	\sim 1100 (forward)			bias polarity	[24], [26]
Si-on-insulator	~ 1100	10 ⁻³	No	Fixed	[54]
FinFET technology					
Si nanocrystals	700–900	10 ⁻³	Yes	Fixed by	[55], [56],
in SiO ₂				fabrication process	[57]
Strained Si-Ge	1200–1600	10^{-2}	No	Fixed by	[58], [59],
				stoichiometry	[60], [61]
Er-doped Si	1530–1540	10 ⁻³	No	Fixed by	[55], [62]
				fabrication process	

TABLE I PERFORMANCE COMPARISON OF SI-BASED LIGHT-EMITTING DEVICES IN LITERATURE

for electronic driver/read-out circuits. Pushing the limits of silicon based light sources, therefore, helps in miniaturizing such sensors and provide a low-cost alternative for coarse and rapid testing of food/water quality and plant health, where high precision is not critical.

V. CONCLUSION

We reported the first proof-of-principle of optical absorption sensing of pigment in solution with a broad-spectrum silicon micro LED designed in a standard silicon-on-insulator CMOS technology. Vertical optical transmission through a glycerol micro-droplet containing a chlorophyll based pigment (sodium copper chlorophyllin) was measured with a silicon photodiode. The on-chip silicon LED was driven in both forward and avalanche modes of operation, which steered its electroluminescent spectrum between visible and near-infrared, without replacing the droplet. The effective absorption coefficient and consequently the concentration in solution were determined from the color ratio (COR) of the measured photocurrent and the molar absorption coefficient of the pigment; the results were validated with a spectrophotometer. We validated our sensor further by employing it as a non-invasive chlorophyll sensor for stress monitor in plant leaves. Light emitted from the LED propagates through the leaf diffusely and undergoes absorption by the cellular chlorophyll before being detected by the photodiode. The COR of the photocurrent was shown to vary linearly with the decrease of chlorophyll from the leaf. Our work demonstrates the viability of a CMOS-integrated silicon LED, as a light source for micro-volume optical sensing.

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