A Novel Flexible Chemical Imaging Set-Up of Amorphous-Si-Based Light-Addressable Potentiometric Sensor by Video Projector

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Abstract:
In this work, a novel set-up of Light-Addressable Potentiometric Sensor (LAPS) for chemical imaging is demonstrated. Present set-up takes the advantage of PC interface facility by utilizing a commercial video projector as a programmable scanning light source. It delivers an easy flexible technique to control the shape, size, movement and as well as the modulation frequency of the measurement spot in user-defined manner. This discarded the complexity of using X-Y stage or multiple light sources for scanning the LAPS surface. Furthermore, atomic layer deposition (ALD) technique is adopted to deposit HfO$_2$ thin film as a sensing membrane on amorphous-silicon based LAPS structure and a pH sensitivity of 59.42 mV/pH is achieved. Finally, the chemical image of a pattern is successfully displayed where 9,990 measurement spots are addressed by programming the light spot in this set-up without any mechanical movement.

Key words: light addressable potentiometric sensor, video projector, amorphous-silicon, pH sensitivity, chemical imaging

Introduction
Light addressable potentiometric sensor (LAPS) is found to be an important semiconductor based label free sensing tool to visualise a two dimensional distribution of chemical species due to its unique capability of addressing sensing sites by modulated light source [1,2]. It was first introduced by Hafeman et al. in 1988 [3] by combining scanned light pulse technique (SLPT) [4] with electrolyte-insulator-semiconductor (EIS) capacitance based sensor. The local photocurrent in the LAPS structure is generated by focusing modulated light source at the desired position on the LAPS surface. A dc voltage is applied to develop depletion layer at the insulator-semiconductor interface in LAPS chip. Now, when the modulated light as local stimulus is applied to illuminate the semiconductor surface, the electron-hole pairs are generated inside there and an ac photocurrent is induced as a consequence of the electron hole pair separation in the electric field in depletion layer. The amplitude of this photocurrent is influenced by the width of the depletion layer at that illuminated point. Therefore by monitoring the ac photocurrent of LAPS, any change in the analyte concentration can be obtained directly in spatial manner [5, 6].

This photosignal at each measurement spot can be mapped into color representation and utilized as a "pixel" to generate the chemical image of the electrochemical properties at the LAPS surface. A chemical image with high resolution will deliver more information about sensing surface. This spatial resolution of LAPS based chemical image depends on the light spot size and the minority carrier diffusion length of semiconductor layer. Different approaches like thinning bulk silicon, using GaAs substrate, amorphous silicon (a-Si) substrate have been attempted to improve the spatial resolution. Among them a-Si is found to be an important material because of having small diffusion length of 120nm [7]. This LAPS based imaging technique has been already successfully adapted to visualize the biological activity of biological systems such as Escherichia coli [8], enzyme [9] and as well as to monitor the ionic diffusion in electrochemical systems [10] and multi ion imaging [11].

The light addressing technique in LAPS set-up is found to be an important issue in the sense of flexibility, miniaturization and speed of measurement system. The conventional approach utilizes mechanical X-Y stage and focused laser beam to address measurement spot one by one on LAPS surface. But this
method suffers from bulky in size and slow measurement speed due to the size and speed limitation of the positioning stage. In another approach, multiple light sources with each having their individual modulation frequency are illuminated simultaneously and the photosignal is extracted for each measurement spot by fast Fourier transformation (FFT) algorithm [12]. Although this approach significantly reduces the measurement time but it has drawback of having limited number of light source. Very recently, digital light processing technology (DLP) was employed as scanning light source in LAPS set-up to generate chemical image with free definition of light spot [13]. However, this technique uses ARM-based processor to access internal digital micro-mirror, which gives rise to a complicated set-up for most users. In this study, a commercial video projector with a projection lens is utilized, where the shape, size, movement and modulation frequency of the light spot can be programmed easily with computer-aided control. This measurement system does not require any complicated mechanics and optics. Besides, an amorphous-silicon based LAPS structure is selected because it works properly in the visible wavelength and serves high-resolution for chemical imaging [14].

Experiment:
Projector based LAPS set up: Fig. 1 represents the schematic illustration of the present LAPS set-up. In this set-up a commercially available video projector is used as a light source and placed just below the LAPS chip. Along with this, a projection lens is installed in between the projector and LAPS chip to focus the image from the projector on the LAPS surface. The measurement spots are defined by the images that are drawn on PC by using standard software and finally projected on the sensor chip though the projector. The position, size, shape, movement and modulation frequency of the light spot are freely executed by programming the images via PC interface. This simple set-up delivers an enormous versatility to the LAPS measurement technique and discards the complexity of using X-Y stage or multiple light sources. The resulted photocurrent from the chip is amplified and then sampled and recorded with a 16-bit data acquisition card (PCI 6221, National Instrument, Germany) by home made LabView based programme on PC. The waveform nature of the generated photocurrent is detected by using a preamplifier (DLPCA 200, FEMTO, Berlin, Germany). For photovoltage vs. reference bias measurement, a bias voltage sweep was generated through DAQ card and applied to LAPS by using a commercially available Ag/AgCl reference electrode. For chemical imaging, a photoresist is used to make “U” pattern on the LAPS surface. Then a programmed light spot is used to scan on the LAPS surface.

Fabrication of LAPS chip: Fig. 2a shows the details of process flow to fabricate a-Si based LAPS structure. 10 nm thick HfO₂ as a sensing membrane was deposited on a-Si/ITO/glass substrate by atomic layer deposition technique (ALD). Next, HfO₂ and a-Si were selectively removed by reactive ion etching (RIE) process for bottom ITO contact. Finally, a Polydimethylsiloxane (PDMS) package was used as a buffer solution container.

Fig.2. Process flow and cross-sectional view of HfO₂/a-Si based LAPS chip.

Results and Discussion:
XRD of HfO₂:

Fig.3. XRD data for as deposited HfO₂ film on a-Si by ALD.
The X-ray diffraction (XRD) pattern of the deposited HfO$_2$ on a-Si is shown in fig. 3.

Optimization of modulation frequency: The waveform of the photocurrent from the LAPS chip at different frequency is depicted in fig.4. In this present set-up, size, shape and modulation frequency of the light spot was programmed on PC and then the image was focused on LAPS surface through the video projector. As a result the maximum modulation frequency of the light spot was limited by the refresh rate of the video projector used. In present set-up, the used projector has refresh rate 60Hz. So that, this present set-up can deliver a maximum modulation frequency of 30Hz which is half of the refresh rate of the projector. It is possible to generate higher modulation frequency with availability of higher refresh rate projector in this set-up.

pH sensing: To test the pH sensing performance of sensor chip with present set-up, a square shaped white spot of size 180X180$\mu$m$^2$ and modulation frequency of 30 Hz was used to measure amplitude of photoresponse as a function of reference bias voltage for different pH value of buffer solutions.

The corresponding photoresponse versus reference bias voltage curves for the different buffer of pH2-4-6-7-8-10 is depicted in fig. 5a. The horizontal shift with pH value is due to the change of surface potential at the interface of sensing membrane (HfO$_2$) and solution with different concentration of H$^+$ presence in pH buffer solutions. To calculate the sensitivity and the linearity, the shift was plotted against pH value and is shown in fig 5(b). The sensitivity of the measurement can be estimated by using following equation,

$$\text{Sensitivity} = \frac{\Delta V}{pH}$$ (1)

where, $\Delta V$ is the change in reference bias due to the change in pH at constant photovoltage. A pH sensitivity of 59.42 mV/pH and linearity of 99.92% was determined, which is close to the Nernstian shift. The constant-bias measurement at 0.56 volt is also achieved with present set-up and is depicted in fig. 6.

Chemical Imaging: A photocurrent image of a photoresist pattern “U” on the LAPS chip is recorded by scanning the LAPS surface and is shown in fig.7.

During scanning, a square shaped light spot of size 170X170 $\mu$m$^2$ was used and the corresponding photocurrent for each position was collected under constant bias. The total...
scan area was 4.6 X5.2 mm² and the total number of measurement spots was 9,990. The resolution of the chemical image depends on the spot size for a-Si based LAPS structure. The resolution can be enhanced by using spot with smaller size and further study on resolution improvement is in progress.

Conclusion
In this work, a novel set-up for LAPS measurement has been introduced. A commercially available video projector was employed as programmable scanning light source to provide an uncomplicated way for flexible chemical imaging. The size, shape, movement and modulation frequency of the light spot were simply achieved by PC interface facility. This simple projector based set-up diminished the complexity of using mechanical stage in conventional LAPS measurement system. There was no mechanical movement involved in this present set-up.

Furthermore, ALD deposited HfO₂ was used as sensing membrane on a-Si based LAPS structure. The photoresponse vs reference bias measurement and constant bias measurement were successfully executed with this set-up to test the pH sensitivity of the a-Si based LAPS chip. Finally, a programmed light spot was created using this set-up and by scanning the LAPS surface as pixel-by-pixel manner, chemical imaging was successfully performed. A study of improving the resolution of the image is in progress. This new approach has a great potential to realize an easy, flexible and low cost programmable LAPS set-up for high resolution chemical imaging.

Acknowledgements
This paper was supported by grants from National Science Council, Taiwan (NSC 99-2221-E-182-056-MY3) and Chang-Gung Medical Research Project (CMRPD 2A0091), Kwei-san, Tao-yuan, Taiwan.

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