

Lung cancer cells detection by a photoelectrochemical MoS₂ biosensing chip

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Abstract: This research aims to explore the potential application of this approach in the production of biosensor chips. The biosensor chip is utilized for the identification and examination of early-stage lung cancer cells. The findings of the optical microscope were corroborated by the field emission scanning electron microscopy, which provided further evidence that the growth of MoS₂ is uniform and that there is minimal disruption in the electrode, hence minimizing the likelihood of an open circuit creation. Furthermore, the bilayer structure of the produced MoS₂ has been validated through the utilization of Raman spectroscopy. A research investigation was undertaken to measure the photoelectric current generated by three various types of clinical samples containing lung cancer cells, specifically the CL1, NCI-H460, and NCI-H520 cell lines. The findings from the empirical analysis indicate that the coefficient of determination (R-Square) for the linear regression model was approximately 98%. Furthermore, the integration of a double-layer MoS₂ film resulted in a significant improvement of 38% in the photocurrent, as observed in the device's performance.

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1. Introduction

The human respiratory system is enveloped by the pleura, a pair of muscle tissues facilitating thoracic cavity movement during respiration. The pleural cavity, holding approximately 5-20 ml of fluid, serves vital lubrication and protective functions for the lungs [1–4]. The occurrence of pleural effusion, characterized by excessive fluid accumulation, is differentiated into transudate and exudate types, varying based on etiology [5–7]. Diverse cancers, primarily lung, breast,

and lymph node cancers, can precipitate pleural effusion. Malignant pleural effusion (MPE) often manifests in lung cancer patients during initial diagnoses, with metastatic breast cancer accounting for a significant mortality rate. The significance of accurate differential diagnoses for these effusions underscores their prognostic implications [8–14]. The study of biosensors involves the measurement of a tumor biomarker known as GSH, which is released by tumor cells. The detection of GSH levels is utilized in the identification and characterization of both benign and malignant tumours, hence presenting a novel avenue for potential clinical utilization.

The photoelectrochemical (PEC) reaction refers to the electrochemical reaction that is initiated by the irradiation of light. Upon exposure to light, the energy of the incident photons surpasses the electronic energy gap of the material. Consequently, the electrons confined within the valence band of the material become stimulated and transition to the conduction band, generating electron-hole pairs. These pairs subsequently migrate to the surface of the material, where the samples undergo electrochemical reactions. The present study employs the current sensor as the fundamental framework [15–17]. This particular type of material structure has the capability to utilize a basic electrical measuring instrument for the purpose of electrical measurement. The cost of the detection procedure is comparatively lower, and it offers a reasonably easy, convenient, and fast alternative to general optical measurements. The redoxactive molecule GSH/GSSG is found in large amounts in cells and is very important in protecting them from oxidative stress. Also, the level of oxidation and decrease of GSH/GSSG is a key sign for many illnesses, including cancer, Alzheimer's, and neurodegenerative diseases. So, keeping an eye on GSH/GSSH has gotten a lot of attention, and recently, a number of studies have released some new PEC sensors for finding GSH/GSSG [18–22].

Transition metal dichalcogenide MoS_2 emerges as a promising photoelectric semiconductor due to its unique properties, notably its biocompatibility and tunable energy gap [23]. It is widely recognized as a highly efficient photoelectric semiconductor with a significant specific surface area and a high optical absorption coefficient. The reason for using MoS_2 is that it is closer to the biological environment than silicon wafers and is less likely to cause adverse cellular reactions. In addition, MoS_2 itself can adjust the energy gap and strong light absorption, and use the number of layers of MoS_2 to control it. Consequently, MoS_2 finds extensive application in the fields of photocatalysis and photoelectric sensing [24]. Prior studies have highlighted the efficiency of MoS_2 -based biosensors, especially in visible light responses [25–27].

This work presents a novel biosensor chip utilizing MoS_2 for analyzing lung cancer cell degree of cancerization. Fabricated via chemical vapor deposition on a silicon-based solar element substrate, the MoS_2 thin film integrates with a self-designed serrated interdigitated electrode (SIE) to facilitate carrier transport. Comprehensive microscopic and spectroscopic analyses explore the film's surface morphology. Experimental investigation via PEC reactions focuses on GSH/GSSG redox reactions.

2. Methodology

The experimental portion is separated into two main parts: fabrication and measurement. The fabrication process is further divided into three following steps: electrode fabrication, MoS_2 growth, and cell culture. The photoelectric flow measurement was performed after the fabrication of the electrode and the cell culture counts were accomplished. Figure 1 displays the experimental procedure. A P-type silicon substrate with a thickness of $200\ \mu\text{m}$ was used for the experiment, and MoS_2 was targeted to grow on an n-type silicon substrate as a material that can interact with the cancer cells. During the measurement, when the material element is treated with light, the light energy is larger than the electron energy gap of the material component, so it can excite the electrons bound in the valence band in the material component to the conductive band, thereby generating electron-hole pairs, causing them to jump to the material surface and perform electrochemical reactions with the sample. There are two primary procedures involved in the

overall operation. The initial step entails the occurrence of the photoelectric effect, wherein the illumination of a material element leads to the generation of electron-hole pairs. Subsequently, the second step involves an electrochemical reaction between the electron-hole pairs produced by the photoelectric effect and the sample. The measured light, which is used in this process, uses electric current which serves as the fundamental basis for the detection of many kinds of cancer cells [28,29].

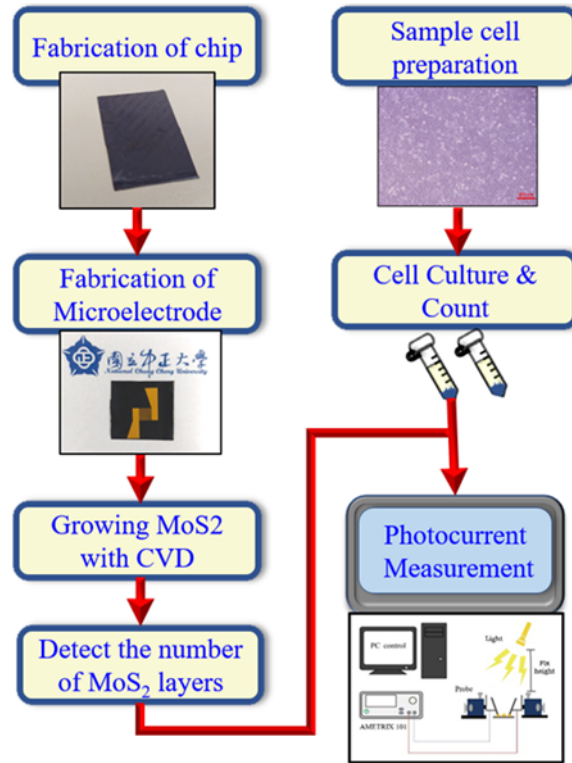


Fig. 1. Experimental flow chart of MoS₂ Biosensing Chip.

2.1. Electrode preparation steps

Figure 2 displays the electrode diagram of the biosensing chip developed in this research. The microelectrode gap has a circular shape with a radius of 100 μm , and it consists of a straight-line interdigitated zigzag electrode. This design aims to quantify the energy localized between the microelectrodes and measure the number of cells. This method exhibits more sensitivity compared to standard electrodes. The flow chart depicted in Fig. 3 illustrates the production process in a comprehensive manner.

Au/Cr electron beam evaporation: Initially, it is necessary to cultivate a coating that is evenly distributed on the purified solar silicon substrate. The primary step in this procedure is subjecting the target to electron beam evaporation in a vacuum setting, which is known as physical vapor deposition (PVD). The high-energy electron beam's kinetic energy is transformed into thermal energy, causing the target material to melt. The heated substance then vaporizes and sublimates, with the resulting gas adhering to the surface of a neighboring substrate to create a thin layer. Regarding the pace at which the substances evaporate, a layer of chromium measuring 20 nm is initially applied at a rate of 1 nm, followed by the evaporation of a 200 nm layer of gold at a rate of 0.2 nm.

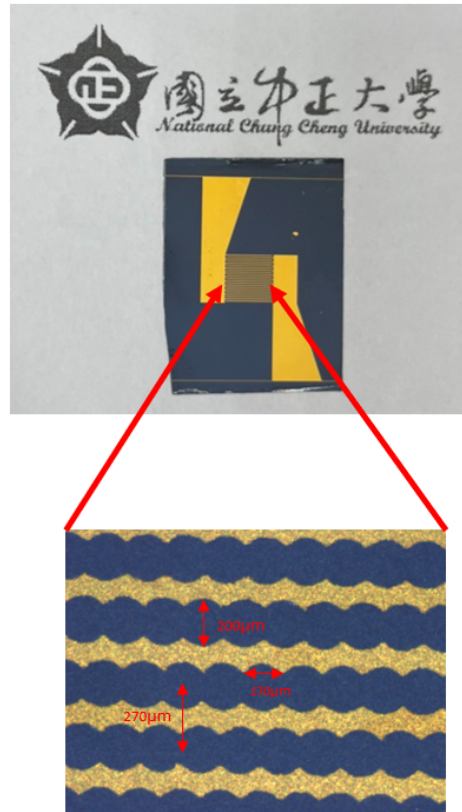


Fig. 2. Straight interdigitated zigzag electrode with 200 μm electrode spacing, 170 μm electrode arc length, and 270 μm optical sensor spacing.

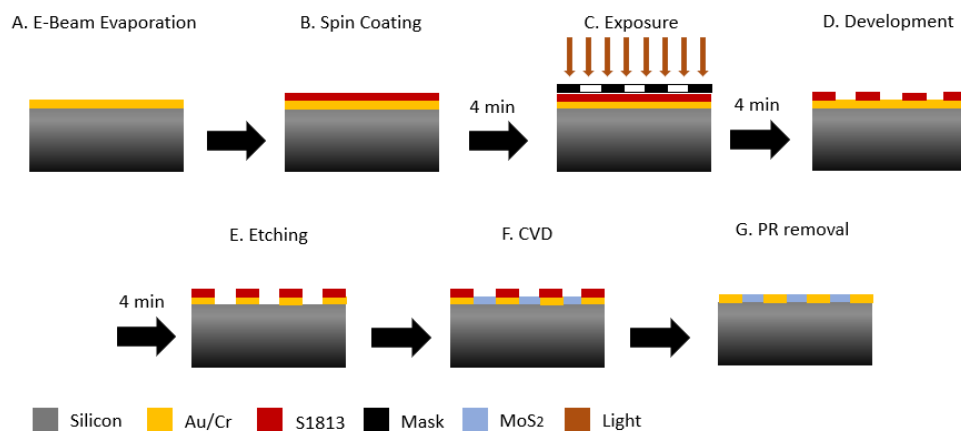


Fig. 3. A. Au/Cr electron beam evaporation, B. Spin-Coating, C. Exposure, D. Development, E. Etching, F. Growth by CVD, G. Photoresist removal.

Application of photoresist coating (Spin-Coating): Secure the solar silicon substrate onto the glass wafer and insert the glass wafer into the photoresist coating machine. Dispense a suitable quantity of *S1813* positive photoresist and evenly distribute it over the surface. To achieve uniform photoresist application on the glass, the coating equipment is configured to operate in two distinct stages. During the initial phase, the rotational speed is adjusted to 700 revolutions per minute (RPM) for a duration of 10 seconds in order to perform spin coating. At this stage, a lower velocity is used for the initial elimination process the surplus *S1813* photoresist; thereafter, at a speed of 1700 revolutions per minute for a duration of 20 seconds spin coating is provided. It can be inferred that increasing the RPM during the second stage allows for a more even spin-coating of the photoresist onto the substrate, resulting in a thickness of approximately 3 μm .

Soft-Bake: Once the process of spin coating the photoresist is finished, it has been positioned on a hot plate set at a temperature of 90°C for a duration of 4 minutes for soft baking. Soft baking serves the function of evaporating the organic solution in the photoresist through heating, hence preventing the photoresist from adhering to the photomask during subsequent exposure. This condition can also result in a more even surface of the photoresist and improve the bonding between the photoresist and the substrate. Inadequate temperature and duration of soft baking can result in excessive retention of organic solution, leading to a loss in the resolution of the exposed pattern. Conversely, it can also reduce the photoresist's sensitivity to light, making it more difficult to develop.

Exposure: The study utilized the UV-KUB3 machine to expose the samples. The exposure position was set at 350 nm, and the needed exposure time was calculated to be 9.3 seconds. Upon exposure to light, the photosensitive agent DQ within the positive photoresist will undergo a photochemical reaction, transforming into ketene. Subsequently, it will hydrolyze into indene-Carboxylic-Acid. DQ, when exposed to an alkaline solvent, will undergo a reaction. The solubility of the unsensitized component is approximately 100 times lower than that of the photoresist. It generates carboxylic acid and enhances the solubility of phenolic resin. The transfer of the mask pattern can be achieved by exploiting the various solubilities of photosensitive and non-photosensitive photoresists in alkaline solvents.

Thermal treatment after exposure: During the process of exposure, a portion of the light that is not absorbed by the photoresist travels through it and reaches the surface of the substrate. The interaction of reflected and incident light waves results in constructive and destructive interference known as the standing wave effect. Irregular variations in light intensity result in the formation of ridges on the surface of the photoresist, leading to alterations in the width of the photoresist lines and impacting subsequent procedures. Hence, subjecting the photoresist to post-exposure baking might induce thermal diffusion, so mitigating any irregularities resulting from the standing wave effect and improving the post-exposure outcome. Both photoresist and unexposed photoresist might exhibit a greater etching ratio when subjected to development. In this procedure, the wafer was subjected to a temperature of 90°C for a duration of 4 minutes following its exposure.

Progress: The photoresist within the region that has been exposed will undergo a transformation into molecules that are susceptible to dissolution by the developer. Thus, in the course of development, the developer will dissolve the exposed area, leaving the unexposed photoresist layer intact. Once the development is finished, it is considered complete. The specialized developer MP351 is utilized for the development of *S1813*. The ratio of MP351 to DI water is 1:4 (v/v). The glass wafer is inserted into the MP351 developer solution and agitate uniformly for approximately 10 to 15 seconds. Lastly, deionized water is used for cleaning to complete the process.

Final Baking: The temperature of this phase exceeded the temperature used for soft baking as the surface will undergo flattening as a result of surface tension. Through the utilization of a 120°C heating plate for a duration of 4 minutes, the medium within the photoresist can

be effectively eliminated. The residual solvent increases the bonding of the photoresist to the silicon wafer surface and strengthens its resistance to corrosion during future etching and ion implantation procedures. Furthermore, the photoresist will undergo a softening process at elevated temperatures, resulting in a molten condition akin to that of glass at high temperatures. The photoresist surface will be smoothed by the influence of surface tension, resulting in a reduction of flaws, such as pinholes, in the photoresist layer. This process effectively corrects the edge profile of the photoresist pattern.

Etching: Etching is the process of adding acidic, corrosive, or abrasive chemicals to the surface of glass. The etching technology employed in semiconductor manufacturing processes can be categorized into two types: dry etching and wet etching. This study uses wet etching as the method for etching. Initially, the wafer is immersed in a gold etching solution for a duration of two minutes. Subsequently, the wafer is extracted and subjected to a thorough cleansing using deionized water. Following the completion of gold etching, the process of chromium etching is carried out in accordance with the aforementioned procedures. A microscope was utilized to continuously monitor the completeness of the electrode pattern.

Photoresist removal: In the last stage, acetone, methanol, and DI water are employed to eliminate the residual photoresist on the wafer, resulting in the completion of the wafer.

2.2. Fabrication of MoS_2

A PEC biosensor made of N-type material, MoS_2 , is used in this study. Chemical vapor deposition (CVD) is used to grow the thin film, which is used to simulate the effect of electron capture on the solar silicon substrate [30,31]. A high-temperature furnace tube is used to heat the mixture to the vaporization point by combining the precursor and the substrate. During the process of vaporization, a chemical reaction takes place resulting in the combination and deposition of MoS_2 onto the substrate made of solar silicon. The procedural sequence used in the experiment is outlined as follows: In order to maintain cleanliness inside the high-temperature furnace tube, it is necessary to address the buildup of sulphur powder and residues on the quartz tube and wafer boat utilized for reactions. To do this, a post-growth procedure including immersion of the wafer boat in a mixture of nitric acid and hydrochloric acid is used. When aqua regia is formed by combining with a volume ratio of 1:3 of HNO_3 and HCl respectively, it undergoes a reaction that effectively eliminates the buildup of sulphur. The reaction period is up to 1 day, and the preceding stages will be continued after the quartz tube has been developed multiple times. After the preliminary work was finished, the weights of the molybdenum trioxide powder (MoO_3 powder) and sulphur powder were measured and placed in the center of the wafer boat. Subsequently, the cleaned solar silicon substrate was placed upside down. Next, the solar silicon substrate is raised or elevated, so that the solar silicon substrate and the MoO_3 are brought into contact to facilitate a chemical reaction so that it produces high quality MoS_2 . Subsequently, the temperature sensor was used to identify and annotate the locations inside the tube where the approximate vaporization points of molybdenum trioxide powder (700°C) and sulphur powder (200°C) were observed. The appropriate duration for heating, the temperature for growth, and the duration of growth were established for the three-zone temperature heating system. Once the establishment of the setup was finalized, the heating system was activated to facilitate the growth of the MoS_2 film. Once the temperature reaches around 200°C , it is possible to activate the high-temperature furnace tube for the purpose of thermal insulation. Subsequently, the device may be removed once it has through a natural cooling process to reach its ambient temperature of 25°C . At this point, it is advisable to keep the samples in a container that is impervious to moisture. Following the completion of the experiment, the designated area had a thorough cleaning process, and further measures were taken to address the consequences. The design diagram of the experimental frame is shown in Fig. 4.

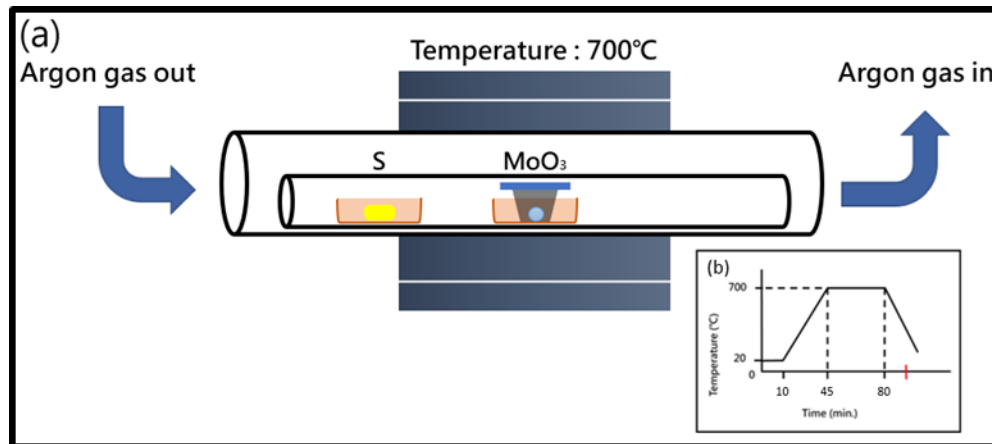


Fig. 4. Experimental setup for MoS₂ film grown by chemical vapor deposition. (a) Experiment configuration diagram; (b) Temperature setting ladder diagram.

2.3. Cell culture procedure

The cancer cell lines used in this study include the CL1 lung adenocarcinoma, the NCI-H460 lung large cell carcinoma, and the NCI-H520 lung squamous cell carcinoma cell lines. The three cell lines exhibit a moderate level of RPM use. Phosphate-buffered saline (PBS) and trypsin are often used in the process of cell dissociation. The afore-mentioned agents were combined inside a water tank maintained at a constant temperature. Subsequently, the temperature of the tank was elevated to 37°C, aligning with the temperature typically maintained within a cell growth incubator. then, the cells were partitioned onto the plates and then subjected to centrifugation. The resulting supernatant was substituted with sucrose, following which the cells were subject-ed to staining and enumeration using a trypan blue solution [29].

2.4. Photocurrent response experiment

The completed wafer underwent an initial cleaning process using deionized (DI) water, followed by drying using nitrogen gas. The probes were fixed using the micro-positioning probe base, followed by contacting the wafer after washing it with deionized water. The micro-probe was affixed to its base to enhance the stability of the probe and minimize any vibrations. The software (Pluse Scan V 1.1) developed by LabVIEW RTE 2013 was utilized to regulate the micro-current count. Additionally, the micro-current meter was employed to supply a bias of 1 V. The experiment was carried out in a dimly lit environment to mitigate any signal instability resulting from the interference caused by an abundance of external light sources. The counting board was initially employed by the experimental cell sample for the purpose of quantifying the quantity, after which it was subsequently inserted into the chip. Subsequently, the chip was retained for a duration of one minute to allow for the stabilization of the signal, hence facilitating the acquisition of error-free data. Once the signal had achieved stability, the light was turn on for a duration of 30 seconds, followed by a subsequent turn off for 40 seconds. This procedure was conducted to evaluate the photocurrent response of the chip, with the data being acquired and recorded using specialized software. The acquired signal was measured, computed, and transmitted to the computer via the data link. Then we use a dropper to drop the prepared cell concentration onto the straight interdigitated zigzag electrodes on the chip. Subsequently, the data was processed using the Origin program in order to derive the photocurrent response of the cell sample.

2.5. Instrumental information

2.5.1. Optical microscope

An optical microscope, often known as OM, utilizes optical lenses to generate a magnified image. The light emanating from the object is amplified as it passes through the objective lens and eyepiece of the optical system. The objective lens disk (Nosepiece) has lenses with magnifications of 5X, 10X, 40X, and 100X. The level of magnification can be adjusted according to requirements. Optical microscopes can be categorized into reflection and transmission varieties based on the design of the condenser and objective, which varies depending on the materials being observed. Reflection microscopes are mostly employed for examining non-transparent samples, with the light source positioned above for illumination. The light reflected by an object enters the microscope to capture an image. This technique is commonly used to observe solids and materials. However, in cases where the sample is transparent or very thin, a transmission microscope is employed. In this type of microscope, light enters from the sample to obtain an image. Typically employed for the examination of biological tissues. The stage is a platform designed to transport and support samples. There is a modifiable aperture located below. To increase the amount of light entering the camera when the environment is dim, the aperture can be adjust to a wider setting.

2.5.2. Raman spectroscopy

Raman spectroscopy is a highly effective technique for analyzing molecular structure, rotational modes, and molecular vibration modes [32]. It is used to explore the determination of crystal lattice and the positions of molecular or chemical bonds. Raman scattering is produced through the interaction of incident light with material. Inelastic scattering arises from the contact between particles. Typically, the laser range consists of visible light, near-infrared light, or near-ultraviolet light. The laser light interacts with the phonons of the molecules, leading to either an increase or decrease in the photon energy of the organic luminescence. To comprehend the MoS₂ film a Raman spectrometer is employed to determine the quantity of layers present. The micro-Raman spectrometer utilized in this experiment is the MRI-1532A model. The micro-Raman spectrometer employs a laser with a wavelength of 532 nm. When the laser beam interacts with the sample, the photons in the laser will collide with the molecules in the sample material, resulting in the production of Raman scattered light. The gadget detects the dispersed light and quantifies the molecular vibrations. An instance of this is the MoS₂ film, which exhibits the vibration modes E₁₂ g and A₁ g. The mode is the primary indicator used to assess MoS₂. The two vibration modes have a strong correlation with the thickness of MoS₂. If the difference in the Δk values between the E₁₂ g and A₁ g peaks is below 20cm⁻¹, the MoS₂ being studied is considered to have a single-layer structure.

3. Results

3.1. Optical microscopic (OM) analysis

In this study, a high-temperature furnace tube system was employed to fabricate MoS₂ thin films on solar silicon substrates by the process of chemical vapor deposition. The OM image in Fig. 5, it demonstrates that the electrode portion undergoes shrinkage as a result of the elevated temperatures experienced during chemical vapor deposition. Nevertheless, according to a series of ongoing investigations, it has been observed that an electrode thickness ranging from 150 to 200 nm does not result in any disruption or the formation of an open circuit within the electrode.

3.2. Field emission scanning electron microscopy analysis

The surface morphology and topology of the MoS₂/c-Si was conducted using FESEM. The electrode exhibits a reduction in size following its growth through chemical vapor deposition at

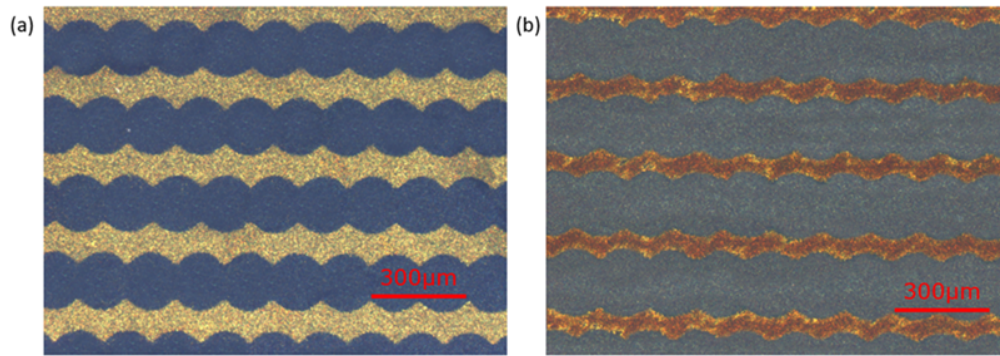


Fig. 5. OM images of electrodes (a) OM image without MoS₂ thin film (b) OM image after growing MoS₂ thin film on the wafer.

high temperatures, as depicted in Fig. 6(a) and 6(b). Moreover, it is observed that the Si substrate exhibits a conical structure, as depicted in Fig. 6(c) which has been coated with MoS₂ as shown in Fig. 6(d). The complete substrate is uniformly coated with MoS₂, with a size of 1 µm as shown in Fig. 6(f).

3.3. Hall effect analysis

The effective carrier concentration in PEC biosensors is influenced by the material's saturation electron velocity and electron mobility. Higher values of both properties result in a greater carrier concentration, leading to increased photocurrent collection. Consequently, the photoelectric behaviour of the biosensors is affected by both carrier mobility and carrier concentration. The magnitude of the present electrical flow is a significant determinant. Prior to conducting measurements, it is essential to ascertain the mean diameter of the joint as well as the thickness of the sample. It is imperative that these dimensions are smaller than the space between the contacts. The experimental findings indicate that the solar silicon substrate exhibits P-type carrier characteristics, with a carrier mobility (μ) of 5.77 (cm²/V. s) and a carrier concentration (N) of 2.2×10^{19} (cm⁻³).

3.4. Raman spectroscopy analysis

The purpose of this study was to analyze the Raman spectrum of MoS₂ in order to get insights into the optical phenomenon occurring between its various layers. Figure 7 illustrates the Raman shift on the X-axis and the strength of the Raman signal on the Y-axis. The Raman spectrum exhibits two prominent peaks at 383.5 cm⁻¹ and 405.7 cm⁻¹, corresponding to the E₁g and A₁g modes, respectively. The E₁g mode arises from the in-plane vibrations of the MoS₂ lattice, involving the oscillation of two S and Mo atoms in opposite directions. On the other hand, the A₁g mode originates from the out-of-plane vibrations of the sulphur atoms, with the atoms vibrating in opposite directions. If the magnitude of the peak difference (Δk) is below 20 cm⁻¹, it can be classified as a monolayer. Nevertheless, if the value falls below 23 cm⁻¹ but remains above 20 cm⁻¹, it can be classified as a dual layer [31]. The experimental findings indicate that the MoS₂ synthesized in this study has a bilayer structure, and the observed peak at 520 cm⁻¹ is due to the presence of silicon [33].

3.5. Quantum efficiency measurement system

The purpose of this setup is to analyze and evaluate the impact of MoS₂ layer growth on the conversion efficiency of the sensor chip. The measurement outcomes are depicted in Fig. 8. The

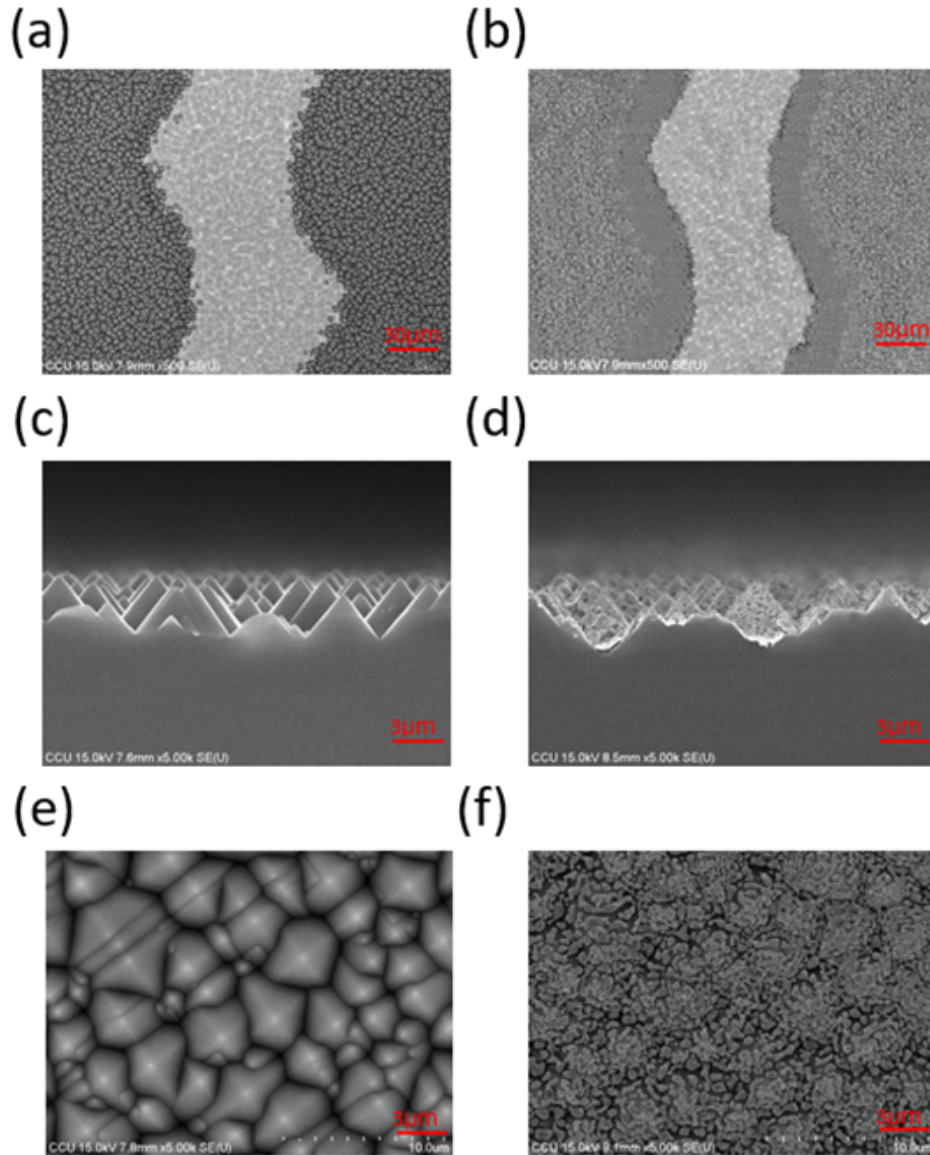


Fig. 6. Component surface topography (a), (c), and (e) are the front view, cross-section, and enlarged view of the original wafer c-Si substrate respectively. Meanwhile, (b), (d), and (f) are the front view, cross-section, and enlarged view of the wafer grown MoS₂ thin film respectively.

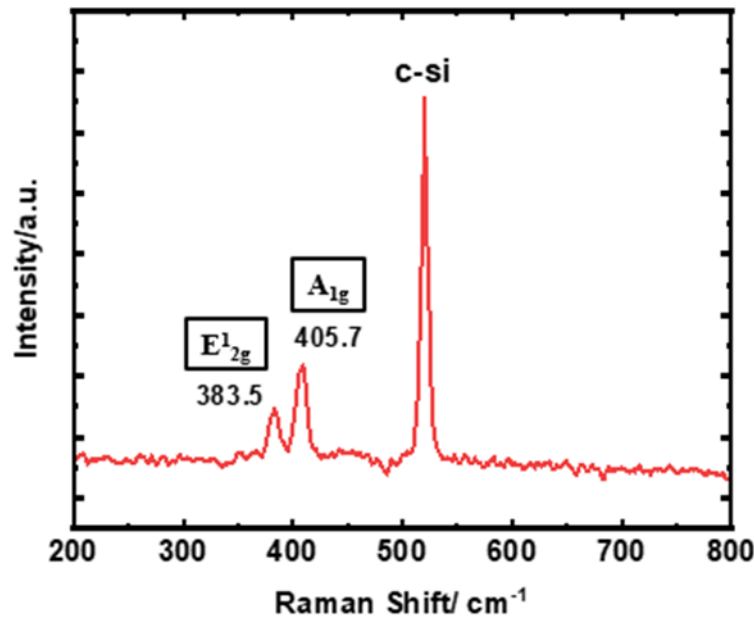


Fig. 7. Raman spectrum analysis of MoS₂/c-Si.

introduction of MoS₂ into the PN junction results in the formation of a more extensive electric field. This enhanced electric field exhibits increased efficiency in decomposing electron-hole pairs following photon absorption. Consequently, the collection efficiency of charge carriers is improved, leading to a greater conversion efficiency [34,35]. The spectrum reveals that the spectral curve exhibits a deeper and closer proximity to the PN junction as the wavelength increases within the range of 300 nm to 500 nm. This phenomenon enhances the conversion efficiency. The band spanning from 500 nm to 800 nm demonstrates the highest conversion efficiency due to the effective decomposition of electron-hole pairs within the electric field of the PN junction following photon absorption. This characteristic reflects the nature of the PN junction. Lastly, the 800 nm to 1100 nm band permeates the lower c-Si layer. The spectrum demonstrates the presence of the P-type in conjunction with the band, and when compared to the sample lacking a MoS₂ layer, it exhibits a broader range of consumption and increased conversion efficiency.

3.6. Photoinduced current measurement

This investigation employs a specific instrumentation method to meticulously examine the spatial distribution of the sensor wafer subsequent to the MoS₂ layer growth. The utilization of a light source calibrated to emit at a wavelength of 532 nm with an intensity set at 80% allows for a detailed analysis [31]. The core focus of this analysis revolves around the assessment of quantum efficiency and resistance pertaining to the photoelectric constituents, coupled with an intricate examination of the absorption and charge dynamics inherent within these components.

Figure 9(a) delineates the discernible reduction in photocurrent observed within the initial substrate, registering at approximately 0.003 mA. Subsequent measurements, taken subsequent to the high-temperature MoS₂ growth, exhibit an identifiable alteration. Figure 9(b) elucidates the transitional boundary between the substrate and the interdigitated layer, revealing a conspicuous divergence in the current flow attributed to the presence of gold and chromium films applied on the electrode surface. Furthermore, Fig. 9(c) presents a comprehensive depiction of the

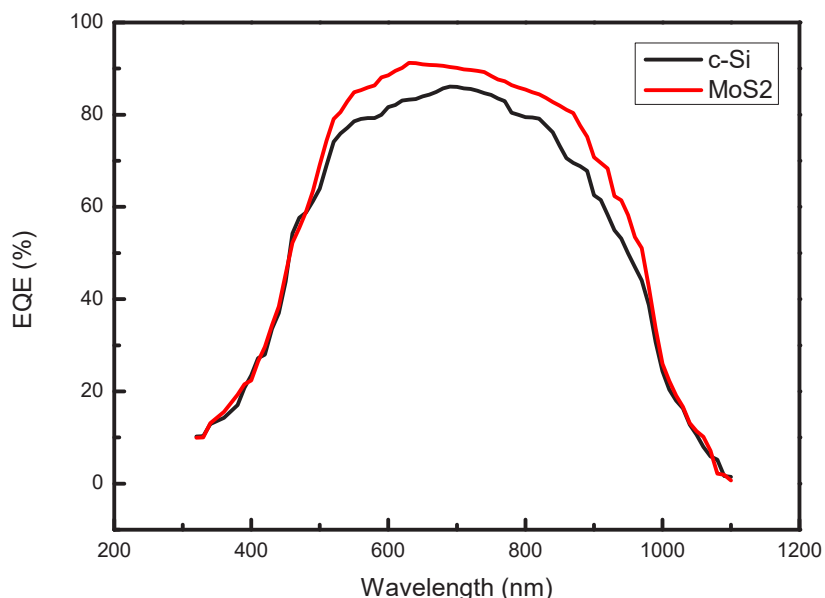


Fig. 8. External quantum efficiency analysis of MoS₂/C-Si.

photoinduced current across the complete c-Si/MoS₂ substrate, characterized by an average range spanning from 0.004 mA to 0.0044 mA. Of significance is a marginal portion of this current, measuring 0.0054 mA, denoting a region where MoS₂ growth is notably comprehensive. This inference is drawn from the consistent diameter of each measured point at 0.01 mm, while the dimensions of MoS₂ span between 0.02 and 0.03 mm. Importantly, the MoS₂ thin film showcases an amplified photocurrent in contrast to the non-grown MoS₂ substrate, indicative of its enhanced photoelectric properties.

Figure 9 effectively illustrates the distinct characteristics across various regions: (a) the C-Si substrate, (b) the interface between the substrate and the electrode post-MoS₂ growth, and (c) the substrate following MoS₂ growth. These maps serve as visual representations, offering insights into the spatial distribution and variation of photoelectric currents within the examined substrate regions.

3.7. Photocurrent response analysis

The concentration catalysis mechanism of GSH and GSSG was employed in cancer cells to verify the detection mechanism of the biosensor that was constructed. In normal cellular conditions, the GSH to GSSG ratio is observed to be more than 10:1. However, in the case of cellular malignancy, there is a reduction in the GSH to GSSG ratio [36,37]. In brief, it can be observed that cancer cells exhibit significantly elevated levels of oxidative stress compared to their healthy counterparts. Consequently, there is a notable rise in the concentration of GSSG, while the concentration of GSH experiences a decline. This disparity in the redox ratio signifies an imbalance [38]. The PEC reaction of N-type structures to GSSG exhibits a significantly higher magnitude compared to the response observed for GSH, as indicated by the prior experimental findings [39]. On the contrary, the PEC reaction of P-type structures to GSH exhibits a significantly higher magnitude compared to the response observed for GSSG [39]. In N-type PEC biosensors, the predominant carriers are electrons, resulting in a more pronounced involvement of GSSG in the PEC reaction process. When subjected to illumination, the interaction of light with a material result in the creation of electron-hole pairs. In this process, the photo-generated electrons join with GSSG,

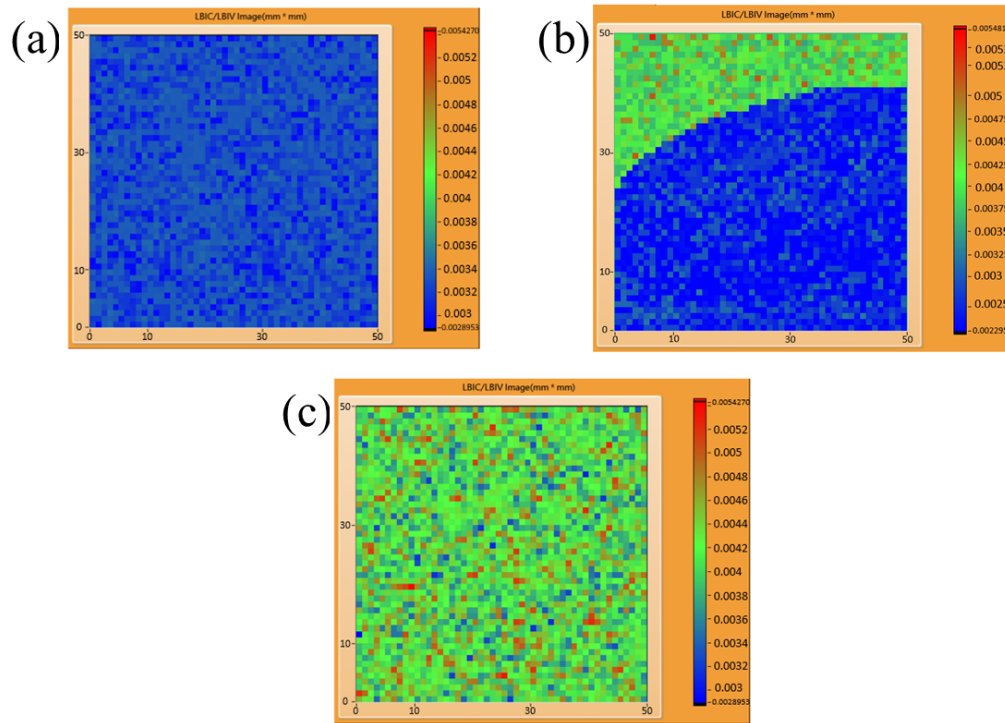


Fig. 9. Photoelectric current maps (a) the C-Si substrate, (b) the junction between the substrate and the electrode after growing MoS_2 , and (c) the substrate after growing MoS_2 .

while the photo-generated holes are detected, thereby establishing a system characterized by the flow of holes. As the severity of cancer progresses, there is an observed increase in the concentration of GSSG within cancer cells, which consequently leads to an increase in the measured photocurrent [19,40,41].

3.7.1. Analysis of MoS_2 /c-Si structure for the detection of GSH

The present study utilizes a MoS_2 /c-Si structure as a fundamental component, where N-type MoS_2 is synthesized on P-type C-Si. The material in contact with the cell solution is characterized as N-type MoS_2 . The aforementioned structure exhibits the generation of electrons upon exposure to illumination. The accumulation of hole pairs and electrons on the N-type MoS_2 side can be attributed to the presence of distinct energy gaps in electron transport. When cancer cells come into contact with the structure, the electrons actively engage in the reduction reaction of GSSG within the cancer cells. The photo response at a given time is directly proportional to the concentration of GSSG, as a larger concentration of GSSG enhances the capacity to effectively separate electrons from holes, resulting in a stronger photo response. The energy band structure diagram is depicted in Fig. 10(a). Once the element is subjected to illumination, the movement of electrons occurs from the valence band to the conduction band. This transition is facilitated by the disparity in energy levels. Consequently, both electrons and holes are conveyed towards the surface, initiating the distinctive reaction of the substance. The addition of a MoS_2 film results in a 38% increase in the PEC signal of the device, as depicted in Fig. 10(b).

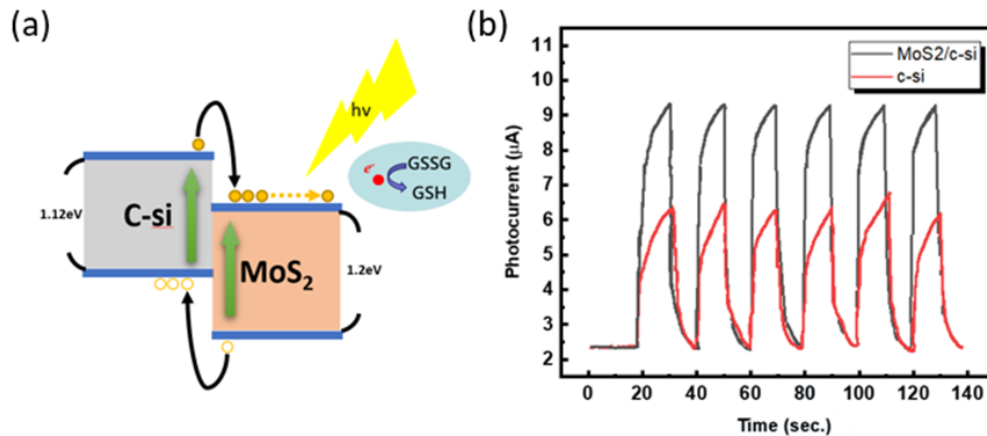


Fig. 10. (a) Schematic diagram of energy bands; (b) Photo response analysis comparison between MoS₂/C-Si and original components.

3.7.2. Analysis of MoS₂/c-Si structure to distinguish the concentration of cancer cells

In this study, the MoS₂/c-Si structure is employed as a constituent for quantifying several types of lung cancer cells. In this study, our main focus was on the evaluation of three distinct lung cancer cell lines. Specifically, we conducted photoelectric flow measurements on clinical samples of three different types of lung cancer cells, namely CL1 lung adenocarcinoma, NCI-H460 lung large cell carcinoma, and NCI-H520 lung squamous cell carcinoma cell lines. Figure 11 shows the photocurrent response measurement results for four cancer cells in tests using a varying number of cells. CL1 is a widely recognized cell line obtained from lung adenocarcinoma, commonly employed in laboratory investigations and preclinical studies pertaining to lung cancer. These cell lines serve as a valuable resource for researchers to explore many facets of cancer growth, genetic alterations, treatment responses, and prospective therapeutic approaches. NCI-H460 is a cell line that originates from large cell carcinoma, a kind of lung cancer. Large cell carcinoma is a subtype of non-small cell lung cancer (NSCLC), comprising around 10-15% of all lung cancer cases. The NCI-H520 cell line is a derivative of lung cancer, specifically categorized as SCC of the lung is a prominent subtype of NSCLC, commonly originating in the bigger airways of the lungs. NCI-H460, CL1, and NCL-H520 are extensively studied and widely utilized cell lines in scientific study pertaining to lung cancer. These types of cells are significant resources for investigating cancer biology, evaluating novel therapeutics, comprehending medication reactions, examining genetic abnormalities, and probing diverse facets of cancer advancement. The photocurrent response curves of the cancer cells at different locations and degrees of cancerous lesions were measured with a microcurrent meter in each test using a different number of cancer cells. As shown in Fig. 11, the relationship between the number of cells and the photocurrent response was linear, and the slopes of the photocurrent responses in cancer cells with different cancer lesions and the number of cells were quite different. Compared with the general optical measurement method, the cost was lower, and the detection process was relatively convenient and fast. The measurement findings of the CL1 lung cancer cell line is depicted in Fig. 11(a). Various quantities of cancer cells were introduced into the measuring solution with a volume of 30 μm. It was observed that the photocurrent exhibited a positive correlation with the number of cancer cells. In the meanwhile, the measurement findings of the NCI-H460 lung large cell carcinoma cell line are depicted in Fig. 11(b). Based on the obtained measurement data, it can be observed that the measured photocurrent exhibits a positive correlation with the number of cells subjected to measurement. The measurement results of lung squamous cell carcinoma NCI-H520 are depicted

in Fig. 11(c). The observed trend in the photocurrent suggests a positive correlation between the density of suspension cells and the involvement of GSSG in the PEC process. Based on the data presented in Fig. 11(d), it can be observed that the various cell types exhibit distinct variations. Additionally, a linear correlation is evident between the variation in photocurrent and the number of cells. The linear regression analysis conducted on the three cell types demonstrates a high level of accuracy, with an R-squared value of up to 99%. The slopes for the three cell lines, namely CL1, NCI-H460, and NCI-H520, are 0.00078, 0.00042, and 0.00116, correspondingly. The equation of the regression curve can be determined by quantifying the size of the photocurrent, which enables the identification of the corresponding cell line among the three options. This approach showcases a cost-effective and relatively convenient detection process compared to conventional optical measurement methods. The discernible differences in photocurrent responses among cancer cells with distinct lesion degrees and quantities hold promise for potential applications in precise cancer diagnostics and monitoring.

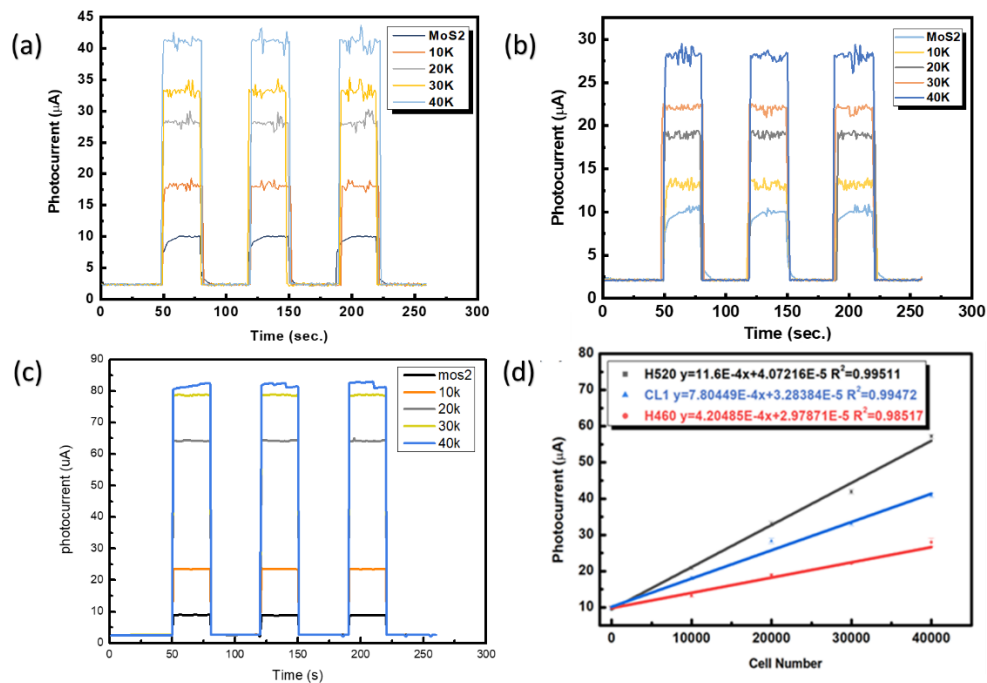


Fig. 11. (a) Photocurrent responses of CL1 under different cell numbers. (b) Photocurrent responses of NCI-H460 under different cell numbers. (c) Photocurrent responses of NCI-H520 under different cell numbers. (d) Three kinds of Linear relationship between photocurrent change and cell number of lung cancer cell lines on a biosensing chip.

The photocurrent response curves exhibited discernible gradients for each kind of lung cancer, highlighting their distinctive attributes. The average standard deviation for CL1, H460, and H520 was 0.5285, 0.49940793 and 0.706856628 respectively, across different cell counts. The minimum standard deviation highlights the effectiveness of our developed biosensor in precisely identifying various types of lung cancer cells. When there were 5000 cells, the standard deviation decreased to 0.3702, 0.5086, and 0.424 for CL1, H460, and H520, respectively. This finding demonstrates the biosensor's exceptional efficacy in accurately detecting the precise type of lung cancer, even when the number of cells is considerably low. In the field of linear regression analysis, the coefficient of determination (R-squared, R^2) is a crucial statistical measure that determines how well the regression model fits the data. The R^2 values achieved for CL1, H460,

and H520 were an impressive 99.472%, 98.417% and 99.5117% respectively highlighting the remarkable predictive capability and dependability of our biosensor across all evaluated lung cancer cell types.

A 1 V bias voltage is applied using a microcurrent meter, while an indoor light source is utilized to stimulate the sample. The incident light will be absorbed by the material, leading to an increase in the quantity of both holes and electrons. Consequently, the electric current will see an increase. The occurrence described is referred to as photoconductivity, wherein the flow of electric current is a consequence of the stimulation induced by the impact of light on a substance. Furthermore, when exposed to light, electrons and holes that have been stimulated by photons will be forced to reposition themselves between the two semiconductors as a result of the inherent electric field. An easily obtainable indoor light source that fulfills the chip development standards can be fixed at a specific distance from the chip. By leaving the sample and establishing a difference in electrical potential at the junction between the two regions, it is possible to cause a decrease in the number of electrons in the n-region and a subsequent increase in the p-region. Currently, when cells are placed on the N-type surface, the electrons will engage in a reduction reaction in GSSG, leading to an increase in conductance. This is due to the fixed number of electrons concentrated on the N side, resulting in an increase in current and the generation of a photocurrent response. The photocurrent response can be utilized to identify the slope, which in turn allows for the identification of the specific form of lung cancer.

4. Discussion

The research involved the deposition of a bilayer of MoS₂ over the light-absorbing substrate of silicon-based solar cells. This bilayer was then integrated with a custom-designed serrated interdigitated electrode (SIE), which facilitates the passage of photogenerated charges. Photoelectric flow measurement was performed on three distinct types of clinical lung cancer cells, namely the CL1 lung adenocarcinoma cell line, NCI-H460 lung large cell carcinoma cell line, and NCI-H520 squamous cell carcinoma of the lung. Subsequently, the phenomenon of shrinkage and separation manifests following the growth of the MoS₂ electrode under elevated temperatures. Upon adjusting the film's thickness to 200 nm, no separation was seen, and only shrinkage occurred, as depicted in Fig. 5 (b). Subsequently, Raman spectroscopy was employed to ascertain the quantity of MoS₂ layers. Based on the observed peak difference of 22.2 cm⁻¹ between E₁² g and A₁ g, it may be inferred that the MoS₂ material exhibited bilayer growth. The composition of our material comprises P- and N-type MoS₂, serving as a transitional layer. The charge carrier nature of the material in contact with the cancer cells being examined is N-type MoS₂. The aforementioned structure induces the formation of electron-hole pairs upon the photoexcitation of charge carriers. Subsequently, the electrons are transported to the N-type MoS₂ region due to the dissimilarity in energy band gaps, resulting in their accumulation in that area. Currently, when the cancer cells that have been quantified are brought into the system, the electrons actively engage in the reduction reaction of GSSG. Hence, it can be inferred that an increase in the concentration of GSSG leads to a corresponding enhancement in the efficacy of electron-hole separation. Furthermore, the utilization of the MoS₂ sulphur vacancy electron capture capabilities significantly enhance the capacity to segregate electrons and holes, consequently augmenting the light response [42,43]. The measurement findings of the CL1 lung cancer cell line is depicted in Fig. 11(a). Various quantities of cancer cells were introduced into the measuring solution with a volume of 30 µm, and it was seen that the photocurrent exhibited a positive correlation with the number of cancer cells. In the meanwhile, the measurement findings of the NCI-H460 lung large cell carcinoma cell line are depicted in Fig. 11(b). Based on the obtained measurement data, it can be observed that the measured photocurrent exhibits an increasing trend with an increase in the number of cells subjected to measurement. The measurement results of lung squamous cell carcinoma NCI-H520 are depicted in Fig. 11(c). The observed trend suggests a

positive correlation between the density of suspension cells and the photocurrent, implying a greater involvement of GSSG in the PEC process. In Fig. 11(d), it is observed that the various cells exhibit distinct alterations, and a strong linear correlation is evident between the change in photocurrent and the number of cells. Consequently, the photocurrent response holds the potential for discerning the specific category of cancer cells.

The photocurrent response curves revealed different and distinctive patterns specific to each form of lung cancer, illustrating their own properties. The discrepancies in the slopes of the curves indicate subtle variations in the behavior of CL1, H460, and H520 lung cancer cells as observed by our biosensor. A noteworthy observation was the continuous and noticeable disparities in the photocurrent responses among different cell quantities. CL1, H460, and H520 cells exhibited similar behaviors, with each cell type showing different responses that remained constant even with an increase in cell numbers. The biosensor exhibited exceptional precision, especially at cell counts as low as 2500. The study successfully distinguished and characterized CL1, H460, and H520 cell types, demonstrating its capacity to reliably separate certain lung cancer subtypes even in situations with few cells. The great level of accuracy achieved when using the biosensor with low cell counts demonstrates its potential as a highly effective tool for detecting cancer in its early stages. Utilizing the coefficient of determination, a qualitative analysis demonstrated an extraordinarily high fit of the regression model for CL1, H460, and H520, each demonstrating a good connection between the observed and anticipated photocurrent responses. The biosensor's reliability in predicting and defining different forms of lung cancer is emphasized in this qualitative assessment.

5. Conclusion

In this study, the relationship between electron-hole transport and GSH was determined by PEC analysis and the structure of N materials. Previously, it was known that N-type biosensors have a higher response to GSSG. There exists a positive correlation between the quantity of cancer cells and the magnitude of photocurrent detected. Additionally, it has been observed that the P-type biosensor has a stronger association with the reaction to GSH. The correlation of the response of the GSSG is higher when the component's surface is an N-type biosensor. Furthermore, an analysis was conducted to examine the correlation between the quantity of modified cells and the resulting photocurrent. The empirical findings indicated that the coefficient of determination (R-squared) for the linear regression model was roughly 98%. Furthermore, the performance of the device exhibited a notable enhancement of 38% in the photocurrent upon the incorporation of a MoS₂ film into the PEC signal. Hence, the future investigation of the GSSG reaction in cancer cells stands to benefit from the effective fabrication of a large-area single-layer MoS₂ film on the substrate, owing to the favorable electrical properties exhibited by the single-layer MoS₂.

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Institutional Review Board Statement. The study was conducted according to the guidelines of the Declaration of Helsinki, and approved by the Institutional Review Board of Dalin Tzu Chi General Hospital (B11201007-1) and the Kaohsiung Medical University Hospital (KMUH) (KMUHIRB-G(II)-20200027).

Disclosures. The authors declare no conflict of interest.

Data availability. The datasets used and/or analyzed during the current study available from the corresponding author on reasonable request.

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