All-silicon photovoltaic detectors with deep ultraviolet selectivity

Yuqiang Li, Wei Zheng* and Feng Huang

* Correspondence: zhengw37@mail.sysu.edu.cn
State key Laboratory of Optoelectronic Materials and Technologies, School of Materials, Sun Yat-sen University, Guangzhou 510275, P. R. China

Abstract

For a practical photodetector, fast switching speed and high on-off ratio are essential, and more importantly, the integration capability of the device finally determines its application level. In this work, the judiciously engineered Si$_3$N$_4$/Si detector with an open-circuit voltage of 0.41 V is fabricated by chemical vapor deposition methods, and exhibits good performance with repeatability. The advanced integration technology of Si$_3$N$_4$ and Si is the foundation for imaging functions in the near future. Compare to the current commercial Si p-i-n photodiodes, the detector cuts off the long-wavelength UV light over 260 nm, realizing the spectrum selectivity without filters or complexed accessories. The stability of this detector is further characterized by cycling response, temperature and light intensity dependence tests. In addition, we also analyze and explain the inherent mechanisms that govern the different operations of two types of Si$_3$N$_4$/Si photodetectors.

Keywords: Photodetection, Silicon nitride, Photovoltaic, Deep ultraviolet, Silicon based

Introduction

High-performance photodetectors with integration potential for imaging are desired in deep ultraviolet (DUV) detection, such as space communication, solar storm observation and atmosphere monitoring [1–3]. Silicon as the most important semiconductor, its photodetection imaging has been demonstrated in the visible and infrared bands, benefiting from its completed growth and processing technology [4, 5]. However, the direct use of silicon in ultraviolet field is prevented by its narrow band gap. The lack of specific absorption for UV light makes silicon inevitably affected by visible and infrared light, curtailing the spectrum selectivity. Attaching a filtering apparatus leads to more complexity, low integration and poor portability of detectors [6]. An important trend in photodetection is to combine DUV sensing materials with silicon readout circuits, enabling working at 0 V bias (photovoltaic), faster response speed and more complicated on-chip signal-processing functions [7].

In current, oxides and nitrides are the materials mainly used for DUV detection (< 280 nm) [8–12]. The oxides usually mismatch with silicon, and SiO$_2$ interlayers or other compounds generate easily during the growth, which may block carrier transport...
and weaken the built-in electric field. Unfortunately, SiO$_2$ itself cannot be used as a proper DUV detection material due to its too large band gap [13]. AlN and BN preparation conditions are too harsh, with etching and integration technologies in their infancy, which leaves a long way from the imaging capabilities of their devices [14–16]. The lack of suitable materials results in DUV photodetection not being used as widely as infrared ones [17].

Based on a large amount of data and meticulous analysis, we realize that Si$_3$N$_4$ as a proper wide band gap material has been neglected. It has a very high level of integration with Si [18]. Si$_3$N$_4$ is usually used as a dielectric or passivation layer, but it also possesses the band gap greater than 5.2 eV and a mature growing-processing technology [19, 20]. Taking Si$_3$N$_4$ as a photosensitive layer combined with Si may be an excellent way to achieve practical DUV photodetector.

In this work, amorphous Si$_3$N$_4$ is prepared on Si by low-pressure chemical vapor deposition (LPCVD) and inductively coupled plasma chemical vapor deposition (ICPCVD) methods. The grown Si$_3$N$_4$ film has a flat surface, pure composition, and appropriate band gap (5.8 eV). Si$_3$N$_4$/Si composite photodetector was further fabricated, which has a photogenerated voltage of 0.41 V and an ultra-fast temporal switching speed. In addition, the detector exhibits a good absorption cut-off edge for incident light. Compared to commercial Si p-i-n photodiodes, it has no response to long-wave UV, fulfilling DUV selectivity. Other systematic characterizations of the device, including switching cycling, temperature dependence and illumination intensity dependence, all indicate a reliable and practical detector.

The switching speeds of the photodetectors consist of LPCVD-Si$_3$N$_4$ or ICPCVD-Si$_3$N$_4$ are distinct under slow response, but tend to be consistent under temporal response. The difference of switching speed is speculated to originate from deep-level defects in the materials, by analyzing the atomic-level morphology and element distribution of the Si$_3$N$_4$/Si interface. The experiments and analysis may provide reference for the construction of other high-performance Si$_3$N$_4$ detectors. In brief, this research broadens the using fields of Si$_3$N$_4$ in photonics, and more importantly, paves the way for the application of DUV photodetection.

Results and discussion

Fifty nanometer amorphous Si$_3$N$_4$ film is prepared on the n-Si surface by LPCVD method at 1200 °C, in which nitrogen penetrates into the interior of Si and react with it. A series of characterizations for the Si$_3$N$_4$ film are implemented. The cross-sectional scanning electron microscope (SEM) morphology of Si$_3$N$_4$ is shown in Fig. 1b, revealing a clear and straight interface, which is further reflected in high-resolution transmission electron microscope (HRTEM) image (Fig. 1c). Atomic force microscope (AFM) results show that the Si$_3$N$_4$ film has an ultra-flat surface with root mean square of roughness only 0.76 nm, advantageous for establishing high-performance detectors [21, 22]. Through further analysis of energy dispersive spectroscopy (EDS) mapping and X-ray spectroscopy (XPS), it can be confirmed that the element distribution of Si$_3$N$_4$ is quite uniform, and the N, Si elements are in the accurate valence state. The peak positions of N$_{1s}$ and Si$_{2p}$ are located at 397.63 eV and 101.88 eV respectively [23]. The absorption spectrum of Fourier transform infrared (FTIR) spectroscopy also proved that in this Si$_3$N$_4$, only the
vibration of Si-N bond exists, which reflects the high purity of the film [24]. The band gap of the grown Si$_3$N$_4$ is estimated to be around 5.8 eV by UV-visible transmission and absorption spectrum, which meets the requirements for being a DUV sensitive material (supplementary information S1). It is based on such high-quality Si$_3$N$_4$ film that practical DUV photodetectors are expected to be demonstrated.

Taking the consideration of energy band calibration, metal platinum and indium are deposited on Si$_3$N$_4$ and Si, respectively, as the positive and negative electrodes. The vertical device structure is shown in the inset of Fig. 2. The 20 nm thin platinum layer is designed to be used as a translucent electrode, which not only guarantees a transmittance of more than 60% in the full band, but also has an excellent conductivity (S2). Correspondingly, the I-V characteristics of the photodetector in dark and 185 nm illumination are plotted in Fig. 2. The device exhibits an ultra-high switching ratio of more than $10^3$ and an open-circuit voltage of 0.41 V, which ensures the practicality for detecting [17]. It can be seen from the figure that the dark current does not show obvious rectification characteristics, which is due to the huge resistance of Si$_3$N$_4$ in dark condition [25], that is, the resistance of Si$_3$N$_4$ has a greater influence on dark current than the heterojunction in this device. The current between metal and semiconductor is larger than the dark current over one order of magnitude at the same voltages...
(shown in S3), implying the metal-semiconductor junction is not the main component of built-in electric fields.

In order to verify the authenticity of the photogenerated voltage, a switch cycle test of the detector at 0 V bias is conducted, as shown in Fig. 3a. The photocurrent rises and falls as the light turned on and off at the 0 V bias voltage, indicating that the device is indeed a working photovoltaic detector, realizing self-driven DUV detection. Besides, the device also displays good stability in cycle test. It maintains similar performance during the illumination continuous switching on and off. From a single switch process (Fig. 3b), the difference in the speed of photocurrent rising and falling is observed. The rise time is larger than the fall time, and the rising photocurrent is composed of two parts, fast and slow response. The phenomenon originates from trap defects in the material and instability of the light source [26, 27]. Incident light excites the electrons in the valence band of Si$_3$N$_4$ to the conduction band and generates free carriers. It takes a long time to reach equilibrium after being captured and then released by trap defects, causing the slow response [28]. In addition, limited by the experimental conditions, the 185 nm light slowly increases to the maximum intensity after turned on, resulting in a slower speed of photocurrent rising than falling. Using a laser as light source can eliminate the interference in the cycle test [10]. Temporal response characteristics of the detector are further characterized to explore the fastest speed (S5). The switch of the detector under the laser only takes 38 μs. We take view that the variation in response speed under two kinds of light sources, is due to the different switching speed of light source and also trap defects.
in Si$_3$N$_4$. In temporal response test, the defects are not excited, leading to a short time of rising photocurrent.

We explored the photoresponse of this detector at different bias voltages, as shown in Fig. 3c. The photocurrent rises super-linearly as the bias voltage increases, which is consistent with the typical volt-ampere characteristics. Unlimited increase of bias will cause detector breakdown [29]. The response speed is relatively slower at 0 V, but fluctuates within an interval (around 10 s) under other bias. Because the bias voltage accelerates the carriers drift and sweep them out of the depletion region to contribute to photocurrent [27]. It also shows that the switching speed of the detector saturates at a small bias voltage.

Dependence of the detector on light intensity and temperature is given in Fig. 4. With the enhancement of illumination, the photocurrent and the open-circuit voltage first increase rapidly, and then tend to saturate. Increased incident photons excite more electron-hole pairs, which contribute to improved photocurrent and built-in electric field. However, as the light intensity keeps increasing, the absorption of photons by the Si$_3$N$_4$ film is saturated, and it cannot generate more photo-generated carriers, which leads to saturation of the current and open-circuit voltage, meanwhile making the responsivity (R) and external quantum efficiency (EQE) decrease accordingly. The definition of R and EQE follows the reported work [30]. The responsivity formula is $R = \frac{I_{\text{photo}}}{(A \cdot P_{\text{inc}})}$, where $I_{\text{photo}}$ is the photocurrent, A the photoactive area, and $P_{\text{inc}}$ the

![Fig. 3](image-url) Time-dependent response of the detector at a series of bias voltage. a Multi-cycle time-dependent photocurrent of the detector at 0 V bias, under 185 nm illumination of 295.4 μW/cm². The current has been taken as an absolute value, same as below. b Single time-dependent photocurrent at 0 V bias. The rise time and fall time are 19.3 and 1.8 s, respectively. Here, the range from $I_{\text{min}}$ to 90% of $I_{\text{max}}$ is defined as rise time, and the range from $I_{\text{max}}$ to 10% of $I_{\text{max}}$ is defined as fall time. c Time-dependent photocurrent at a series of bias voltage under the fixed 185 nm light power density of 295.4 μW/cm². d Dependence of photocurrent and rise time on bias voltage. Red zone indicates the range of rise time, under the bias voltage from −2 V to −8 V.
incident light power. The calculation of EQE can be expressed by \( \text{EQE} = \frac{hcR}{q\lambda} \), where \( h \) is Planck’s constant, \( c \) the speed of light, \( q \) the electron charge, and \( \lambda \) the incident wavelength. The detector exhibits a good responsivity of 0.325 A/W and an extremely high EQE of 218%, under an illumination intensity of 3.2 \( \mu \text{W/cm}^2 \) and a bias voltage of \(-5\) V. However, EQE decreased to 3.07% under \( 0 \) V bias, indicating that the external electric field has a significant effect on suppressing carrier recombination. In this work, the Si\(_3\)N\(_4\) film is only 50 nm, and its ability to absorb light is not strong enough. We speculate that a suitable thickness of Si\(_3\)N\(_4\) film can optimize the detector’s linear response interval versus light intensity.

From 78 K (liquid nitrogen temperature) to 350 K, the I-V characteristics of the device are characterized. The open-circuit voltage decreases linearly with temperature, shown in Fig. 4f, which is due to the effect of temperature on carrier diffusion. The photogenerated voltage depends on the built-in electric field, which relies on the

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**Fig. 4** Dependence of the Si\(_3\)N\(_4\)/n-Si detector on light intensity and temperature. a) I-V characteristics of the Si\(_3\)N\(_4\)/n-Si photodetector with light power density from 3.2 to 295.4 \( \mu \text{W/cm}^2 \). b) I-V characteristics from Fig. 5a with extended axis (0 to 0.8 V) to clearly show the open-circuit voltage. c) Dependence of the open-circuit voltage and responsivity versus light intensity. Open-circuit voltage is extracted at 0 V bias, and responsivity is extracted at \(-5\) V bias. d) Dependence of photocurrent and external quantum efficiency versus light intensity. e) I-V characteristics of the Si\(_3\)N\(_4\)/n-Si photodetector with varying temperature from 78 K to 350 K. f) Linear dependence of the open-circuit voltage on temperature.
contact potential difference, and it can be described as $V_D = \frac{k_B T}{q} \ln \left( \frac{N_A N_D}{n_i^2} \right)$. $V_D$ is the contact potential difference, $k_B$ the Boltzmann constant, $T$ the temperature, $q$ the electron charge, $N_A$ the acceptor concentration, $N_D$ the donor concentration, and $n_i$ the intrinsic carrier concentration. With other parameters fixed, $V_D$ varies linearly with $T$, which is consistent with the experimental fitting results.

Based on the analysis of the $\text{Si}_3\text{N}_4$/Si heterojunction, $n$-Si and $\text{Si}_3\text{N}_4$ theoretically form a larger contact potential difference compared with $p$-Si, thereby providing a higher photo-generated voltage [19, 31]. The band diagram and experimental results can be seen in S6. They are qualitatively consistent with each other, and the deviation of values is attributed to the interface states and shifting Fermi level of $\text{Si}_3\text{N}_4$ from the intrinsic position [3, 32].

The detector’s DUV selectivity is demonstrated by spectral response test (Fig. 5). It cuts off obviously in the long-wave UV region (> 260 nm), which cannot be achieved by current commercial silicon photodiodes, complementing the lack of detectors specially used for DUV. Therefore, it will be not necessary for $\text{Si}_3\text{N}_4$/Si detectors to add filtering apparatus or signal separation equipment. Study for improving the suppression ratio is ongoing.

In two methods, LPCVD method obtains a $\text{Si}_3\text{N}_4$ layer through nitriding silicon wafer via $\text{N}_2$, and ICPCVD method deposits $\text{Si}_3\text{N}_4$ onto the silicon surface by reacting $\text{NH}_3$ with $\text{SiH}_4$. The two types of $\text{Si}_3\text{N}_4$/Si composite detectors do not differ much in characterizations, except for the response speed. The ICPCVD-$\text{Si}_3\text{N}_4$/Si detector reached the

**Fig. 5** Spectral photoresponse of the $\text{Si}_3\text{N}_4/n$-Si photodetector and $\text{Si}$ p-i-n photodiode. Responsivity of the $\text{Si}_3\text{N}_4/n$-Si photodetector and commercial $\text{Si}$ p-i-n photodiode measured at diffraction wavelengths ranging from 190 to 300 nm, under the bias of $-5$ V and 0 V, respectively. The dash square denotes the distinction of two detectors’ responsivity in the 260–300 nm region.
saturation state more quickly in the time-dependent response test, as shown in Fig. 6a. However, further temporal response indicates the switching speeds tend to be similar under the ultrafast 193 nm pulsed laser. The element distribution and lattice at the interface are analyzed (Fig. 6c) to explore the underlying mechanism. The nitrogen element line scan perpendicular to the interface direction shows that both the two types of Si$_3$N$_4$ cut off well at the interface and do not diffuse into silicon, indicating the response speed difference is not due to the non-uniformity of built-in electric fields. HRTEM shows that the interface of LPCVD-Si$_3$N$_4$ is flatter, but the shaded area indicates defects possibly. In this work, we take the point that in ICPCVD method, the hydrogen element in the growing sources (NH$_3$ and SiH$_4$) has the effect of passivating trap state defects [33, 34], making the photo-generated carriers saturate faster, which shortens the slow response process. This is consistent with the analysis of switching speed mentioned above in Fig. 3.

Conclusions

In this work, compact and flat Si$_3$N$_4$ film is prepared by the CVD methods, and integrated with Si to fabricate DUV detectors. Its temporal switching takes only 38 μs. Compared with commercial silicon p-i-n photodiodes, the cut-off response to long-wave UV light of Si$_3$N$_4$/Si detectors indicates the designed selectivity for DUV, rather than a broad band. This detector exhibits a good responsivity of 0.325 A/W and a high EQE of 218% at −5 V bias. A range of characterizations including cycling switching test, energy band calibration, temperature and light intensity dependence tests all imply a reliable and efficient device. The distinction of response speed between the LPCVD-Si$_3$N$_4$/Si and ICPCVD-Si$_3$N$_4$/Si detectors is also explained by analyzing the interface defects, which provides a reference for the further preparation of other high-performance detectors. In general, this research lays a foundation for the development of applicable DUV imaging photodetectors and provides the theoretical basis.
Methods

Si$_3$N$_4$ film growth: LPCVD method took nitrogen as N growth source, which reacted with silicon at 1200 °C to form amorphous Si$_3$N$_4$. The LPCVD-Si$_3$N$_4$ film was purchased from Nanjing MKNANO. Tech. Co., Ltd. In ICPCVD method, NH$_3$ and SiH$_4$ reacted at 300 °C forming Si$_3$N$_4$ film, and the flow ratio between NH$_3$ and SiH$_4$ was 14: 10.5. The ICPCVD deposition system is a Plasma lab System 100 ICP180 from Oxford Instruments Plasma Technologies.

Device fabrication: a round Platinum electrode with the radius of 200 μm was deposited on Si$_3$N$_4$ surface by ion sputtering. The thickness of Platinum layer is 20 nm. Then, thermally fused indium was plated at the side of Si as the back electrode.

Material characterization: The AFM image, cross-sectional SEM morphology, EDS and chemical composition mapping were characterized by CSPM 5500 and ZEISSAURIGA Focused Ion Beam etching system. The XPS pattern were collected by an X-ray photoelectron spectroscope (Thermo Fisher ESCALAB 250Xi). The FTIR spectrum and transmittance spectra was conducted by Fourier infrared spectrometer (Shimadzu IRAffinity-1S) and UV – VIS spectrophotometer (Shimadzu UV-3600). The nitrogen element line-scan and HRTEM test was performed by Tecnai G2 F30 of FEI (300 kV).

Device measurements: The 185 nm monochromatic light was obtained from the spectral line of a quartz-packaged low-pressure mercury lamp through an optical filter, and the light power density was measured by the VXUV20A photodetector from Opto Diode Corp. The I-V characteristics of the device were measured by using Keithley 4200 source meter, equipped with a temperature-adjustable platform and a vacuum chamber. The temporal responses were measured by a 6G oscilloscope, KEYSIGHT DSOS604A, whereas the 193 nm pulsed light was from GAMLASEREX5/250 mini excimer laser. The DUV spectral-response test system used Shimadzu UV-2600 as continuous adjustable light source, with KEITHLEY 2636b as SourceMeter.

Supplementary information

Supplementary information accompanies this paper at https://doi.org/10.1186/s43074-020-00014-w.

Additional file 1. Includes: Section 1. The plot of ($αhν$)$^2$ as a function of incident photon energy ($hν$) into Si$_3$N$_4$; Section 2. Characterizations of platinum electrodes; Section 3. I-V characteristics of the metal-semiconductor junctions; Section 4. Schematic diagram of transient response test; Section 5. Temporal response of the detector; Section 6. I-V characteristics of the Si$_3$N$_4$/n-Si and Si$_3$N$_4$/p-Si detectors, and the energy band diagram.

Abbreviations
DUV: Deep ultraviolet; LPCVD: Low-pressure chemical vapor deposition; ICPCVD: Inductively coupled plasma chemical vapor deposition; SEM: Scanning electron microscope; HRTEM: High-resolution transmission electron microscope; AFM: Atomic force microscope; EDS: Energy dispersive spectroscopy; XPS: X-ray spectroscopy; FTIR: Fourier transform infrared; R: Responsivity; EQE: External quantum efficiency

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Authors’ contributions
W.Z. and F.H. conceived and directed this work. Y.L. performed the experiments. Y.L. and W.Z. discussed the results. Y.L. drew the pictures and wrote the manuscript. The author(s) read and approved the final manuscript.

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