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Development and Performance Study of Perovskite Graphene Photodetector

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Abstract: *Due to the lack of gain mechanism and poor light absorption ability of graphene, it is difficult for single-chip graphene photovoltaic devices to obtain high photovoltaic conversion efficiency. In view of this bottleneck, this paper aims to solve the above problems by preparing heterostructures with perovskite materials in graphene. The transfer process of graphene film was optimized to reduce the p-type doping of graphene field effect transistor and significantly improve its mobility. Polymethyl methacrylate technology is applied to the graphite process to solve the problem of channel carbonized photoresist residue in semiconductor devices. In addition, vertical graphene nanowalls (GNWs) were fabricated on Si substrates by radio frequency plasma enhanced chemical vapor deposition (RF plasma enhanced CVD), and then perovskite / GNWs hybrid photodetectors were obtained. The experimental results show that the device has high sensitivity and stable performance. In the wavelength range of 635 nm, the reaction speed of the element reaches 3.2 × 10^5 A / W, and the response time is 24 ms (descending edge) to 8 ms.*

Keywords: *perovskite, graphene, photodetector, field effect*

1. Introduction

At present, there are many new graphene / perovskite composite light detectors, based on the high mobility of graphene carrier and perovskite has good ability to capture light. In 2004, Andre Gam and Professor Constantine Novoselov of Manchester University in the UK have made breakthroughs in the field of graphene[1] . Graphene has a unique band structure with a mobility of nearly 200 times higher than that of traditional silicon materials and a wide spectral light absorption range. These excellent properties make it widely used in semiconductor devices, optoelectronic devices and solar cells. However, due to its small absorption cross section, fast recombination speed and imperfect gain mechanism, its sensitivity to single-photon crystal is reduced. Perovskite is a new type of semiconductor material. Due to its high absorption rate, absorption band from ultraviolet to near infrared, direct band gap, adjustable band gap and other excellent properties, perovskite materials have become the focus of optoelectronic research. The disadvantages of graphene photodetectors can be compensated by integrating perovskite materials into graphene photodetectors to prepare graphene / perovskite materials. Therefore, this paper will develop a new graphene / perovskite quantum field effect transistor based on perovskite field effect products and perovskite quantum dots. Since the 1950s, silicon gene has become the first batch of semiconductor materials in microelectronics due to its rich raw materials, stable chemical properties and wide applications. Silicon-based diode and transistor have strong compatibility, can integrate photoelectric signal, digital image and a variety of technologies into a small chip. However, with the shrinking of the device volume, the energy consumption and heating of the device have become an important problem restricting the development of the device. In recent years, thanks to the rapid development of nanotechnology, feasible methods have been proposed to solve the above problems. Compared with flat graphene, vertically oriented graphene film has good mechanical stability and high internal conductivity, especially its porous structure and high surface volume ratio, which makes the separation efficiency of electrons and holes higher. Plasma Enhanced Chemical Vapor Deposition (PECVD) is a chemical vapor deposition technology that improves the activity of the reaction material in the vacuum chamber by glow discharge of the reaction gas, so that it can react at low temperature to obtain solid film. This technology has been widely used in the industry. Especially in the growth process of the film, the required temperature is lower than that of the chemical vapor deposition (CVD)[2] .

In this paper, a simple and universal method was used to prepare a new type of metal-halide

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graphene nanowall / perovskite photodetector by RF-PECVD (Radio Frequency-Plasma Enhanced Chemical Vapor Deposition) method. The graphene nanowall with high quality was directly grown on (SiO_2 / Si) substrate, etched GNWs, electrode deposition, and perovskite spin coating.

2. Overview of graphene photodetectors and perovskite photodetectors

2.1. Overview of Graphene Photodetectors

Although graphene has a wide absorption area, its light absorption is only 2.3 % under the longitudinal irradiation of light. Although graphene has zero band gap characteristics, it has large spectral detection ability. Therefore, the sensitivity of graphene-based photodetectors is limited to 10^{-2} A / W[3]. In order to improve the performance of the whole device, scholars have adopted three ways to strengthen the light absorption ability of graphene. The first is to achieve the functionality of graphene. The second method is to enhance the light absorption ability of graphene by changing its structure and combining it with the light structure. The third is the combination of graphene and photosensitive absorption materials. At present, domestic and foreign scholars have explored metal contact, heterogeneous structure composite and plasma enhancement. The following is a description of two commonly used graphene photoelectric detection devices.

Graphene photodetector based on integration is a new type of graphene optoelectronic module developed by using micro-nano optical elements and graphene materials. In 2012, Vienna University of Technology combined the Fabry-Perot microcavity[4] with the graphene photoelectric detector, so that its ability to absorb light increased from 2.3 % to 26 times (> 60 %), and the photosensitive response rate of the graphene photoelectric detector with this composite structure reached 21 mA / W. Vienna University of Technology produced a new photoelectric detector in 2013 and combined it with the structure of silicon optical waveguide. The light absorption of the device increased significantly, and the light absorption reached 44 %. The grating technology is used in the light-induced grating pressure enhanced graphene photodetector, which can reduce the composite efficiency of graphene and prolong its service life, so as to produce a high-gain graphene photodetector. Figs. 1 show the structure of the composite photoelectric detector made by the Spanish Institute of Photonics combining PbS colloidal particles with graphene in 2012[5] .

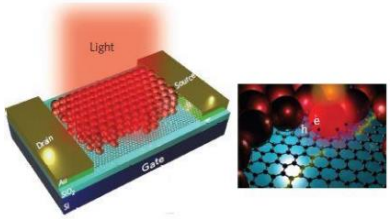

Figure 1: Photodetector with graphene/quantum dot composite structure

2.2. Overview of perovskite photodetectors

Perovskite has high light absorption rate and good carrier transfer performance, so it has broad development prospects in solar cells, photodetectors, LEDs and other aspects. In 2014, Xie Yi team spin-coated $MAPbI_3$ film on polyethylene terephthalate (PET) flexible substrate with ITO electrode pattern to form ITO / $MAPb_3$ / ITO coplanar device[6] . It can be detected in a wide range of 310 – 780 nm, but its reaction rate is not high. 2015, Zhang and other papers on MAPbI3 ; the effect of membrane shape on the performance of detector is discussed. They added MACl with different molar mass to the perovskite precursor solution of $MAPbI_3$, thus transforming $MAPbI_3$ from dense membrane to island network structure. It is found that the island surface has a larger surface, which increases the light scattering and absorption rate, and increases the luminescence current.

3. Preparation and Characterization of Monolayer Graphene

3.1. Transfer graphene film

In the SiO_2 / Si transfer graphene film, the most common method is the wet chemical etching substrate method[7] . Due to the low thickness and weak microstructure of monolayer graphene,

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wrinkles, cracks and fractures are easy to occur during transmission. In order to ensure that the graphene transfer process adopted can achieve the optimal characteristics of the device and reduce the influence of impurities on its doping, it is necessary to make it have good continuity and no pollution and defects. Polymethyl methacrylate (PMMA) is used as a flexible support film. The following is the specific steps for transferring graphene films :

A drop of water was dropped on the PET substrate, and the copper flakes grown by monolayer graphene were cut into thin slices. The copper flakes were evenly placed above the substrate, and the water was dried by filter paper, and then pasted on paper. PMMA (methyl methacrylate solution, ethyl lactate as solvent, 960 K, 4 wt %) was spin-coated onto the surface by homogenizer to solidify[8] ; then, the structure of PMMA / graphene / copper foil was removed from the substrate by tweezers and heated at 100 ℃ for 5 min to make PMMA dry through. Preparation of hydrogen chloride : hydrogen peroxide : water volume ratio of 2 : 1 : 20 solution, in the solution impregnation PMMA / graphene / copper foil structure, remove copper base. Place it in the solution for about 10 minutes, then fix the back of the copper foil on a dry, wet glove with a clamp and remove the graphite layer on its surface. After removing the copper base, deionized water was used to remove residual hydrochloric acid and hydrogen peroxide. The PMMA / graphene film was then immersed in acetone for 30 min, rinsed repeatedly with deionized water, and dried with nitrogen. The silicon thin plate is cut to about 1.1 cm × 1.1 cm, cleaning the surface (with detergent, deionized water, acetone, alcohol, each cleaning 20 minutes). Put the silicon film under PMMA / graphene, and then gently lift it to ensure the smooth sample. The specimen shall be inclined to be fully dried until there is no water stain. Place it on the heater, heat treated at 120 ℃ for 20 minutes, and completely bonded with silicon substrate. After the PMMA was demoulded, the matrix was placed in isopropanol for 30 min, repeatedly dipped in isoacetone, cleaned, and then dried with nitrogen.

3.2. Performance characterization of monolayer graphene

After the graphene film was prepared, the morphology of graphene surface was studied by optical microscope and scanning electron microscope (SEM), and the morphology was analyzed.

Optical microscope analysis: Although the graphene single crystal has only one atomic thickness, its structure can be seen on the silicon surface of any SiO_2 by monochromatic light observation. In the case of visible light, the SiO_2 of 300 nm and 100 nm thickness is selected as the best material by optical microscope observation, so as to achieve rapid detection of the material[9] . Through the experimental study, it was found that graphene materials were prepared by graphene technology. The material surface has no residual, no wrinkles, cracks, pores and other defects. The graphene has not yet fully grown into a film, so the difference between it and the substrate can be seen.

SEM characterization: Fig. 2 (a) shows the SEM images of graphene films prepared on 300 nm SiO_2 / Si substrate. As shown in the figure, the graphite core is hexagonal and its surface thickness is about 50um × 50um. The experimental results show that the morphology and size of graphite films are related to the flow rate and partial pressure ratio under various growth conditions, and the morphology and size are related to the flow rate and partial pressure ratio of CH_4 / H_2. Figure 2 (b-d) is the SEM images of graphene films under different growth states.

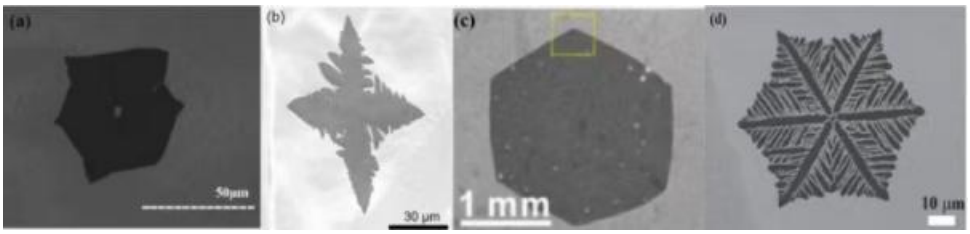

Figure 2: SEM of monolayer graphene under different growth conditions

4. Preparation and performance characterization of graphene photodetectors

4.1. Preparation of Graphene Photodetectors

Fig. 3 is the schematic diagram of back-gate GFET structure. Firstly, a heavily doped Si substrate was selected as the back gate electrode, and 300 nm SiO_2 was used as the insulating medium. On this basis, the contact between the growing electrode and n-type silicon was prevented to some extent.

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Using PECVD method, large-scale, continuous graphene film as channel. Finally, the simplest back-gate GFET is prepared by depositing metal copper at both ends of the graphene channel as the source and drain electrodes.

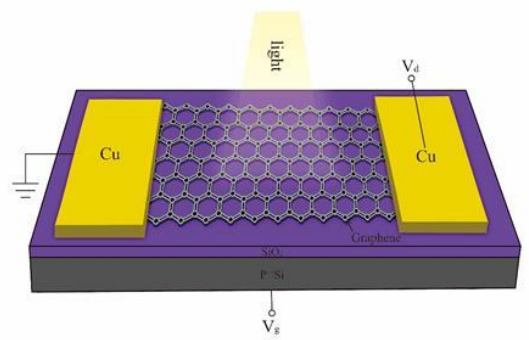

Figure 3: Structure diagram of back-gate GFET

The existing manufacturing process is improved to achieve high reliability integrated GFET manufacturing. The specific preparation process : First of all, the graphene film is transferred, the specific steps are referred to 2.1. In order to combine the graphene film with the substrate better, the monolayer graphene was transferred to the SiO_2 / Si substrate and annealed at 120 ℃ for about 20 minutes. Then the photoresist film evenly spin coating, spin coating placed in 100 degrees Celsius environment for drying. The target substrate coated with photoresist was aligned with the electrode mask in the exposure machine, and the sample after exposure was immersed in the developer solution. Then deionized water was used to rinse, blow and dry[10] . Subsequently, the electrode preparation operation required a layer of 5 nm chromium and a layer of about 40 nm gold on the sample. Finally, PMMA and photoresist AZ3100 were rotated and coated on the gas in order, and the samples were photolithographed with a moving mask exposure device to make it develop. A group of graphite films were etched into a group of separated strips through the oxygen plasma etching process to separate the devices on the same liner to eliminate the mutual interference between the devices. The PMMA was removed by dipping with 3 % sodium hydroxide for 5 min and acetone. and finally leads to the back gate of the third end.

4.2. Performance characterization of graphene photodetectors

Volt-ampere characteristics of GFET: Fig. 4 shows the volt-ampere characteristic curve of the device under 0 V gate voltage with or without illumination. V_{ds} ranges from − 1 V to 1 V. It can be seen that the output curves are straight before and after light irradiation, indicating that there is a better ohmic connection between graphene and metal before and after light irradiation. Although GFET has a linear relationship before and after light, its slope changes with light. After light irradiation, the slope of the output curve increases, indicating that the resistance value of the device is low, which is reduced from 249 Ω in illumination to 201 Ω. There is no current saturation in the test area, indicating that the device has a high load voltage.

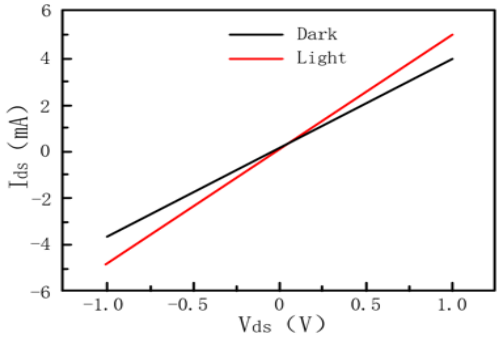

Figure 4: Voltammetric characteristic curve of GFET

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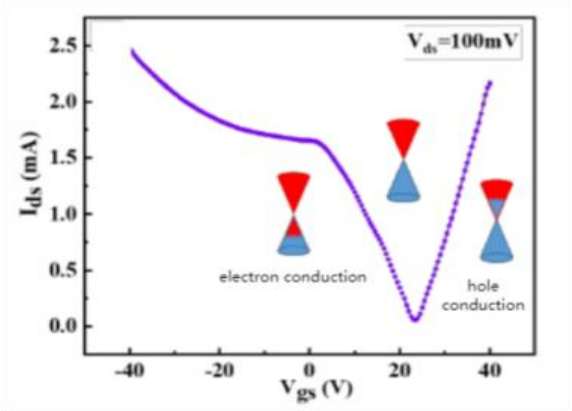

Figure 5: Transfer characteristic curve of GFET

Transfer characteristics of GFET : Figs. 5 show the transmission curve of graphene FET under the source-leakage bias voltage of 100 mV. The transmission characteristic curve is determined by the change of carrier density in the graphite channel, and this curve shows typical bipolarity. The gate voltage corresponding to the minimum value of source and drain is also known as the Dirac point voltage (V_{Dirac}), which is a key voltage for graphene conductive conversion[11] . When $V_{Dirac} > 0$ V, graphene exhibits p-type doping ; when $V_{Dirac} < 0$ V, it exhibits n-type doping ; when $V_{Dirac} = 0$ V, the carrier content is the smallest and shows the characteristics of electrical neutrality.

The experimental results show that when the voltage V_{gs} is − 40 V to 40 V, the carrier concentration of the electrode will first decrease and then increase. It can be seen from the graph that the Dirac point is about 23 V when the carrier density is the largest. The left side of the Dirac point is a hole and the right side is an electron. Dirac point should be 0 V. However, graphene is susceptible to environmental factors such as atmosphere and substrate. The Dirac point here will deflect to the right, because it is exposed to the air and it is easy to absorb water and oxygen from the air.

5. Study on Graphene Nanowall Technology and Its Growth Mechanism

5.1. Preparation of GNWs and verification of their growth mechanism

As shown in figure 6, The experimental process of preparing graphene nanowalls : using acetone, alcohol and deionized water to clean the substrate for about 10 minutes. After cleaning, dry with high purity nitrogen. Put into the reaction chamber of PECVD. When the pressure is less than 3 Pascal, H_2 is introduced as a protective gas and the gas flow is about 10 sccm. After the pressure of the reaction chamber reaches a certain degree, the temperature regulation system is started, and the heating time is set to be 45 min to 700 ℃. When the temperature rises to 700 ℃, the CH_4 gas is introduced, and then the H_2 and CH_4 flow rates of 4sccm and 6sccm are adjusted to stabilize the pressure. Turn on the RF power supply, adjust the power to 200 W, while minimizing the back sputtering power. At this point, nano graphene sheets began to pull up. About 30 minutes later, the access of RF power, heating power and CH_4 gas was closed one by one. The sample was removed when the temperature of the reaction chamber dropped to room temperature by continuously injecting protective gas H_2.

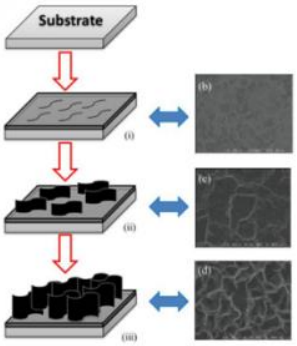

Figure 6: Schematic diagram of vertical graphene nanowall growth process

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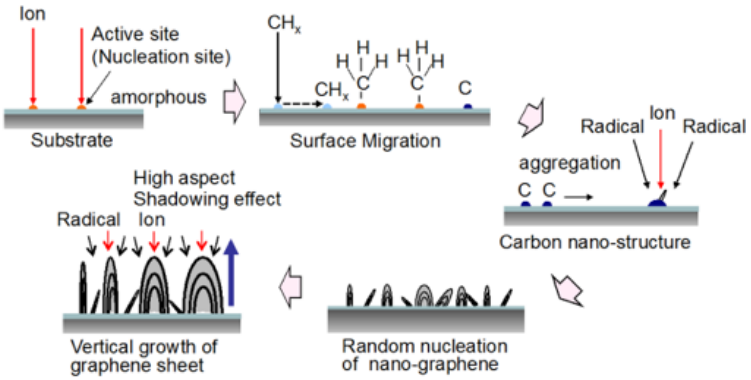

Figure 7: GNWs growth mechanism

As shown in figure 7, The growth mechanism of GNWs: At first, the substrate will adsorb carbon-containing groups to form a very thin, amorphous carbon layer, and then react on the ultrathin carbon layer to form graphene nanoislands. On the graphene nanoislands, high-energy plasma has a significant role in promoting the absorption of carbon groups. When multiple factors act, the high growth rate of nanoparticles is greater than its wall thickness, which makes the graphene nanoisland deformed and forms smaller graphene nanoplates. The carbon group in the plasma has a sufficient surface expansion rate, so that its free radical expands perpendicular to the electrode plane. In another case, the lower graphene layer is covered by a higher vertical layer. Results: In short graphene sheets, the content of activated carbon materials decreased, and the growth stopped, and a high vertical graphene nanowall was formed. With the extension of the growth cycle, the longitudinal nanowall of graphene diffuses continuously, and finally a complex structure-nanowall is formed in the nanostructures. The longer the growth period is, the larger the distance between the nanowalls at the tip is, and the saturated state is finally achieved. A two-dimensional graphene film is formed on the substrate surface. In a stable growth state, the length of nanotubes increases linearly and maintains its shape.

5.2. Preparation of GNWs / Perovskite Photodetectors

Specific steps of perovskite synthesis: 0.3 mol methylamine solution with equimolar hydroiodic acid. Then, stir in ice bath for 60 minutes, then stir in water bath for 30 minutes, and finally remove the water bath, and continue to stir for 60 minutes to get CH_3NH_3I solution. Then the mixture was poured into a clean container and placed on the heating plate to heat and vaporize to obtain ammonium methyl iodide crystals. Finally, the obtained methyl ammonium iodide was recrystallized with ethanol-ether to obtain pure methyl ammonium iodide powder. $PbCl_2$, PbI_2 and CH_3NH_3I crystal powders were dissolved in dimethylformamide solution at the molar ratio of 2.2: 0.5: 0.5. The perovskite solution was obtained by fully stirring under sealed and shading conditions.

Preparation of device operation steps: using the method of evaporation electrode experiment. The electrode takes Au at about 40 nm as the main body, and a layer of Cr is coated on the sample before the gold plating operation to enhance the adhesion of Au on the silicon wafer. In order to better separate the devices integrated on the same substrate and avoid mutual interference between devices, the carbon wall was etched by oxygen ion etching process to make it separate into a series of strips. Then the device was placed on the homogenizer for perovskite spin coating operation. After the spin coating operation is completed, the device is removed from the homogenizer and annealed on the heating plate (condition : the temperature is 100℃). Then, a vertical graphene nanowall / perovskite photodetector can be obtained.

5.3. Performance evaluation of GNWs / perovskite photodetectors

Characterization of GNWs / Perovskite Composites: The morphology of GNWs / Perovskite Composites deposited on graphene wall and single layer graphene was compared by SEM technology, and good film-forming properties can be seen from SEM morphology (a-d). The compactness of perovskite film is shown in Figs. 8. The perovskite layer almost completely covers the graphene wall, which indicates that it has a very degree and grain arrangement, and it can be deduced that there are irregular grains on its surface. By comparing the two scanning electron microscopy profiles, it can be

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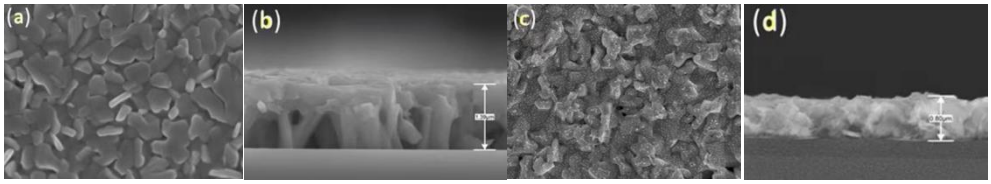
found that the film-forming performance of perovskite on monolayer graphene is very poor. and a large number of pinholes exist on the deposited perovskite; the film-forming performance of perovskite on the graphene wall is good, and there are no holes and other shortcomings. The number of pinholes of perovskite deposited on its surface is also greatly reduced. The existence of a large number of pinholes will greatly affect its absorbance and current.



(a) SEM morphology of monolayer graphene/perovskite films (b) SEM morphology of section of monolayer graphene/perovskite film (c) SEM morphology of GNWs/ perovskite film (d) SEM morphology of GNWs/ perovskite thin film section

Figure 8: SEM morphology of graphene/perovskite composite film

Study on the performance of GNWs / perovskite photodetectors: The performance of the device was tested by simulated solar emitter and Keithley 2450. As shown in the Figs. 9, in the dark state, the output curve is linearly symmetric, indicating that the OM contact characteristics of the metal electrode and graphene are good. Spectrum effect refers to the effective light energy that adds light voltage or current to the device. The response under 0.5 V source-drain bias voltage was tested in the experiment, and it was found that in the detection of the visible band, we can obtain a higher response. With the increase of voltage, the reaction rate will be faster at lower light power density.

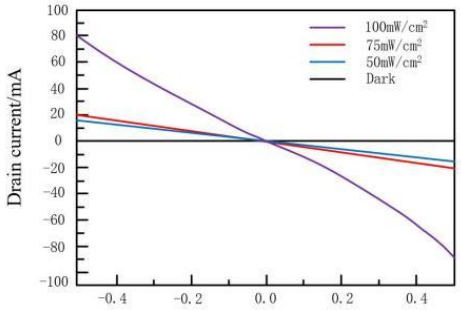


Figure 9: Volt ampere characteristic curves of the device under simulated sunlight

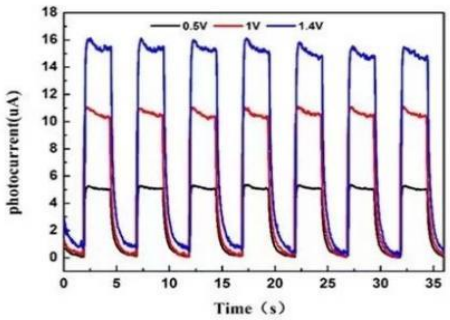


Figure 10: The characteristic curve of photocurrent changing with time at 0V bias, 50uW optical power and 635nm incident light

In the 635 nm simulated sunlight, the reaction speed and reaction speed of the device are very fast. Under simulated sunlight irradiation, the response speed is relatively slow. In order to better study the reaction speed of graphene wall-perovskite photoelectric detector, after obtaining the structure and working principle of the device, we carried out the same bias. Fig. 10 When the bias voltage is 0 V and the optical power is 50 UW, the incident light at 635 nm becomes a square incident light with a period of 10 seconds after the chopper, vertically incident to the graphene wall / perovskite device, and the characteristic curve of photocurrent changes with time. It can be seen from this figure that the detector has good stability and repeatability. In multiple optical switching, the output power remains unchanged, and the response speed is fast, which is comparable to the performance of the ideal device and has no response delay.

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6. Conclusions

Firstly, the high-performance and high-quality graphene field-emitting element (GFET) technology is deeply discussed, and a back-gate graphene FET with excellent performance is developed. Based on the advantages of graphene and perovskite, a graphene / perovskite composite photoelectric detector is successfully developed. In this paper, the photoelectric characteristics and working principle are also discussed in depth. Improvement of graphene wet transfer technology. This paper focuses on the relationship between different etching agents, ammonia doping and different etching agents. In the graph chemical process of graphene, the PMMA intermediate layer technology was used to solve the problem of residual gum material generated by photoresist carbonization under the isoionic bombardment. The electrical properties of the device can be improved by using PMMA interlayer, doping with ammonia solution and selecting appropriate etching agent when etching the substrate. The electrical and internal mechanism of graphene photoelectric detector with field effect are deeply discussed. Through the comprehensive analysis of different process conditions, the fabricated GFET device has stable and repeatable photosensitive characteristics and high reaction rate, which proves its excellent resistance performance with graphite materials and its electric field control effect. A new metal-metal-carbon-graphite-perovskite-perovskite type optical detector was prepared by RF-PECVD technology, which directly etched high-quality silicon nitride material on (SiO_2 / Si) substrate. Experiments show that the instrument has good repetition, stability and continuous switching characteristics, and the output energy is basically unchanged in the continuous conversion process. Its response time is very fast, close to the optimal equipment, and no response delay. Compared with flat graphene films, such a unique mechanical stability, high conductivity, especially its porosity and high volume ratio as a horizontal structure can not only promote the development of GNWs in photoelectric detection, but also show its great benefits in solar cells. With the continuous development of its technology and the continuous improvement of supporting technology, its application scope is becoming more and more wide, and has more important development prospects.

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