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Low-cost Visible-Light Photodetector Based on Ag/CdSe Schottky Diode Fabricated using Soft Chemical Solution Method

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Abstract

The Schottky diode with a configuration of Ag/CdSe/ITO has been fabricated using soft chemical solution method. In this study, uniform nanocrystalline CdSe thin films of about 0.41 μm thickness were grown on ITO coated glass substrate under optimized deposition conditions. X-ray diffraction (XRD) and FESEM studies showed that the deposited thin film exhibit nanocrystalline in nature with hexagonal structure and well defined spherical grains with different sizes. The compositional analysis showed that the CdSe film becomes cadmium deficient and selenium richer. Ag/CdSe/Ag ohmic contact and Ag/CdSe/ITO Schottky diode were fabricated for photodetection study. Current-voltage (I-V) measurements of the synthesized Ag/CdSe/Ag ohmic contact showed good photoresponse to visible light indicated that the prepared structure is suitable for photodetector application. The novelty of this work is to use simple and low cost method to fabricate the Schottky diode with a configuration of Ag/CdSe/ITO. The I-V characteristics of Ag/CdSe/ITO Schottky diode were measured under dark and illumination conditions, and it has been observed that the diode exhibits good rectification property. The as-obtained results highlighted that the fabricated Ag/CdSe Schottky diode could be considered as a promising optoelectronic device that can be effectively used in the visible region.

Keywords: Cadmium selenide, Thin film, Schottky diode, Photodetector, Photoresponsivity.

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Introduction

Photodetectors are essential elements can be applied in space research, optical communications, biomedical imaging, flame detection, night-vision and many other applications, basically has the ability to transform light into electrical signals.[1-3] In the recent years, various wide band gap materials have drawn a large interest to fabricate compact UV-detectors due to their excellent photodetection properties.[2] However, PbS and CdTe have a significant role to play in fabrication of visible wavelength photodetector because of its favorable optical properties.[4,5] In order to overcome the difficulties associated with PbS and CdTe materials such as, the high cost and rarity of indium and tellurium, the researchers are always on the lookout for alternative materials for the fabrication of visible-light detectors. There is many compound semiconductors to replace PbS and CdTe like CdS, CdSe, ZnS, and ZnSe etc. of which CdSe is the best choice because of their potential applications in solar cells, optical detectors, dosimeters of ionized radiation, field-effect transistors, and optoelectronic devices etc.[6] CdSe belonging to the II-VI group can exhibit optical activity in the infrared (IR) and visible region. The distinct properties of CdSe such as a suitable direct bandgap, a high absorption coefficient and high photosensitivity, etc.[7] make it an excellent candidate for a great deal of variety of applications in thin film transistors[8] and optoelectronic devices such as solar cell,[9] light emitting diode,[10] photovoltaic devices,[11,12] sensors,[13] etc. Literature suggests that CdSe thin

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film can form excellent rectifying contact with noble metal such as gold (Au)[14] and graphene.[15] Hence an investigation on the electrical properties of CdSe thin film Schottky diodes is very significant in the context of its applications in optoelectronics.

Al-Kotb *et al*.[14] reported the Au Schottky contact on thermally evaporated CdSe on p-Si (0 0 1) substrate and investigated its temperature dependent electrical characteristics. Zhang *et al*.[15] used chemical vapor deposition (CVD) method to fabricate CdSe NB/graphene Schottky diode. The fabricated structure exhibit excellent rectification characteristics and such photodetector exhibits high responsivity and gain and fast photoresponse speed. Motivated by this, we have fabricated Ag ohmic as well as Schottky contacts on nanocrystalline CdSe thin films synthesized using soft chemical solution method on ITO substrate and studied the photosensing properties of both the devices through I-V measurement.

CdSe thin films can be deposited by different deposition techniques such as spray pyrolysis,[16] vacuum evaporation,[17,18] solution growth technique,[19] physical vapour deposition,[20] pulse reversal plating technique,[21] low temperature chemical bath deposition,[22] galvanostatic deposition technique,[23] electron beam evaporation,[24] chemical Bath deposition[25] and successive ionic layer adsorption and reaction (SILAR) technique[26] etc. Earlier the synthesis, structural and optoelectronic properties of nanocrystalline CdSe thin films prepared on glass substrate by chemical bath deposition route have been reported elsewhere.[25]

We are reporting a soft chemical solution synthesis method for fabrication of CdSe/ITO structure and Ag/CdSe/ITO Schottky diode for visible light photodetector application in the present investigation. Compared with other deposition techniques soft chemical solution method has advantages such as low processing temperature and possibility of large scale deposition etc. We investigate the electrical characterization of CdSe/ITO structure and Ag/CdSe/ITO Schottky diode through current-voltage (I-V) measurements under dark and illumination conditions using Keithley source meter (Model No. 2400).

Experimental Details

Substrate Cleaning

The deposition of the nanocrystalline CdSe thin films has been carried out on commercially available ITO coated glass substrates supplied by Techinstro, Nagpur. The glass substrate coated with ITO was cleaned by using standard process reported by Li *et al*.[27] ITO coated glass substrate were ultrasonicated in soap solution for 10 minutes and then rinsed in distilled water for 20 min. Without drying ITO coated glass substrate were dipped in isopropanol, ultrasonicated in acetone for 10 minutes, transferred to fresh isopropanol bath for 2 minutes, and finally, the substrates dried in air and kept in an airtight container before deposition of the thin film.

Preparation of Nanocrystalline CdSe Thin Film

Soft chemical solution method is basically a chemical deposition technique, which is more advantageous technique because it is a low-cost technique for producing large-area thin films of semiconducting materials, operated at low temperature, and does not required costly instrumentations.[28] This technique is more useful than the other methods because of less incorporation of impurities, deposition of multi-component chalcogenide thin films over a wide range of stoichiometry, high reproducibility, and environment-friendly control of film thickness or stoichiometry by the optimization of various deposition conditions.[29] In this technique, substrates are immersed in a chemical bath containing the chalcogenide source, the metal ion, added base and complexing agent. For the preparation of nanocrystalline CdSe films, selenium powder, sodium sulphite, cadmium chloride and ammonia (AR grade) were taken as initial ingredients. A sodium selenosulfate (Na_2SeSO_3) prepared by following the procedure reported before[30] was used as a source of Se^{2-} ions. In the growth of CdSe thin film from a chemical bath, ammonia is used as the chelating agent to bind Cd^{2+} ions and minimize the speed of precipitate during the growth process. Sodium selenosulphite provides the necessary Se^{2-} ions.

In order to prepare nanocrystalline CdSe thin films, reaction bath contains 10 mL 0.1M $CdCl_2{\cdot}2H_2O$, 3.5 mL of 30% NH_3 aqueous, 10 mL of freshly prepared solution of Na_2SeSO_3 in 100 mL beaker and the rest distilled water to make the volume to 50 mL. On controlling the pH value at 9.5, films of nanocrystalline CdSe can be obtained on ITO coated glass substrates. Well-cleaned ITO substrates were then immersed vertically into the deposition bath against the wall of the beaker containing the reaction mixture. The deposition was allowed to proceed at 70°C for 5 hrs. After that, the substrate was taken out from the bath, washed with deionized water in order to remove surface impurities and loosely bound ions or atoms, then left to dry naturally. The deposited film was reddish in color, well adherent to the glass substrate, and uniformly dispersed over the entire substrate. The scheme for nanocrystalline CdSe films' deposition by soft chemical solution method is represented in Figure 1.

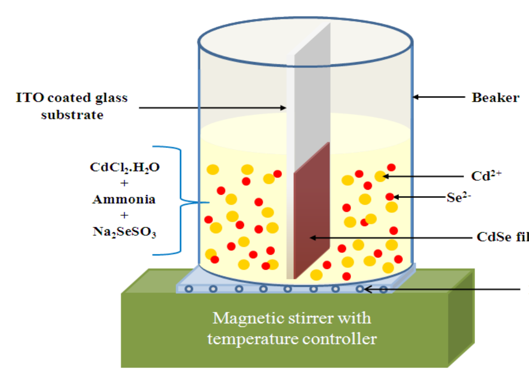

Figure 1: Schematic diagram of the deposition of nanocrystalline CdSe films by soft chemical solution method on ITO coated glass substrate.

Device fabrication

Silver (Ag) contacts were printed on CdSe thin film samples grown on ITO coated glass substrate for preparing two kinds of devices.

Firstly, we present the fabrication of Ag/CdSe/Ag metal-semiconductor-metal (M-S-M) structured visible-light photodetector by printing thin layer of Ag paste on top of nanocrystalline CdSe films as shown in Figure 2. The effective area of the photodetector was estimated to be 1.2 cm^2. In order to study photoconductive and photo-detecting properties, the device is illuminated by visible-light using an incandescent bulb. Secondly, a low-cost visible-light photodetector based on Ag/CdSe Schottky diode was formed by applying thin layer of Ag paste on CdSe/ITO structure. A schematic of the Ag/CdSe/ITO Schottky device structure with electrical contacts is shown in Figure 3. The visible-light sensing properties were measured at room temperature and at ambient conditions.

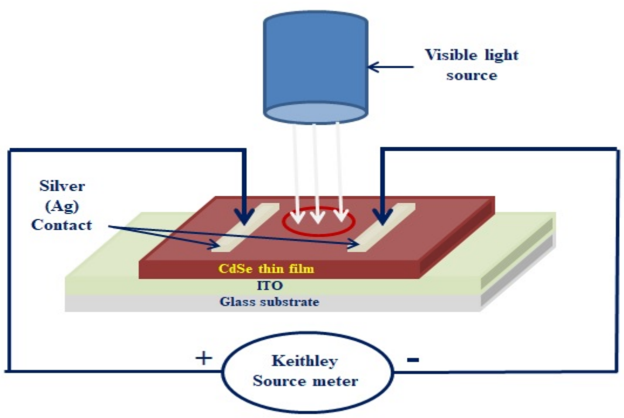

Figure 2: Schematic diagram of Ag/CdSe/Ag metal-semiconductor-metal (M-S-M) structured visible-light photodetector,

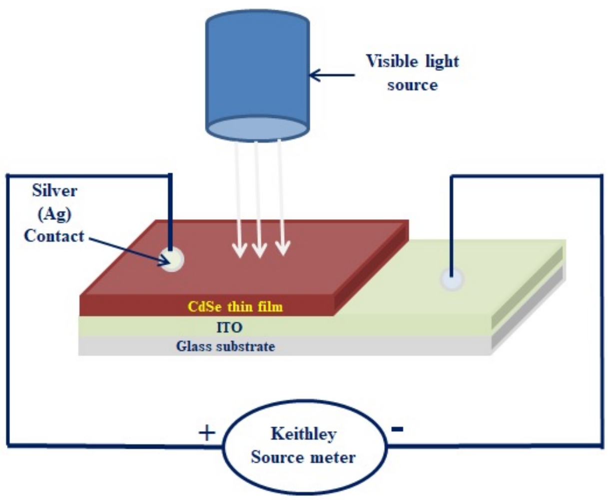

Figure 3: Schematic diagram of Ag/CdSe/ITO Schottky device structure.

Characterization of the Films

X-ray diffraction measurements were carried out using a Bruker AXS, Germany (D8 Advanced) diffractometer with Cu K_α radiations with wavelength 1.5405 Å in the scanning range 2θ=20-80°. S-4800 Type-II (HITACHI high technology corporation Tokyo, Japan) field emission scanning electron microscope (FESEM) was used to determine morphology and elemental chemical composition of the sample. I-V measurement of the Ag/CdSe/ITO Schottky contact was performed using a computer-interfaced Keithley 2400 source measurement unit.

Results and Discussion

Structural Analysis

The X-ray diffraction measurement of nanocrystalline CdSe film grown on ITO coated glass substrate was taken to identify the crystalline structure. The XRD pattern of the prepared nanocrystalline CdSe film onto the ITO substrate is depicted in Figure 4. Several well-defined peaks observed at $2\theta \approx 26.56°$, 33.73°, 42.60°, 54.52° and 78.34° are assigned to (1 0 1), (1 0 2), (1 1 0), (2 0 2) and (3 0 1) crystallographic planes, respectively, of the hexagonal crystal structure of CdSe, in agreement with standard data [31]. Well known Scherrer's formula is used to calculate the average crystallite size and it is found to be 41 nm. So it can be concluded from the XRD pattern that deposited CdSe thin films is nanocrystalline in nature. Four prominent peaks were observed at 37.71o, 51.45o, 61.54o and 65.51o attributed to the ITO substrate. This confirms the formation of CdSe/ITO structure using simple and low-cost soft chemical solution method.

Morphological Studies

Figure 5 shows the FESEM image of the nanocrystalline CdSe thin films deposited on ITO coated glass substrate. FESEM study reveals the uniform distribution of spherical grains of irregular size over the entire substrate surface. A similar

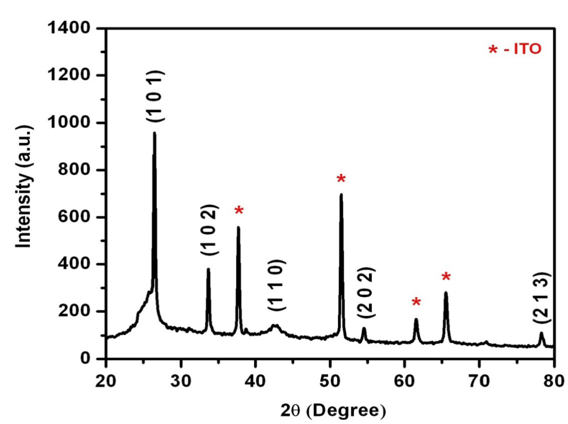

Figure 4: XRD pattern of the nanocrystalline CdSe film prepared onto ITO substrate using soft chemical solution method.

observation was reported by Habte *et al.* [32] for CdSe thin film prepared on glass substrate using malonic acid as a complexing agent. The inset of Figure 5 shows the FESEM image of the nanocrystalline CdSe thin films deposited on glass substrate. This shows that irrespective of the nature of the substrate, there is no significant change in the morphology was observed.

Visible-light Sensing Properties of a Device

To observe the photoconductive properties, dark and visible-light illuminated behavior of Ag/CdSe/Ag M-S-M structured visible-light photodetector shown in Figure 2 is studied. Figure 6 shows the current-voltage (I-V) characteristics curve obtained from CdSe visible-light photodetector before and after visible light illumination. I-V curve of nanocrystalline CdSe films prepared on ITO show linear behavior with respect to Ag as contacts. This confirms the ohmic nature of the M-S-M structure, indicating that the work function of metal Ag is higher than semiconductor CdSe.[33,34] Also, the nature of

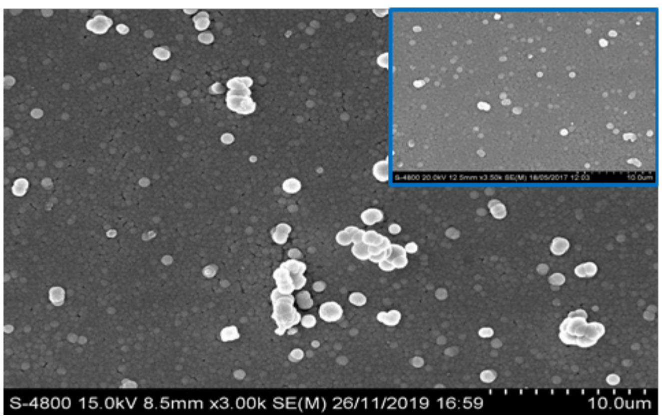

Figure 5: FESEM images of nanocrystalline CdSe film prepared onto ITO substrate using soft chemical solution method.

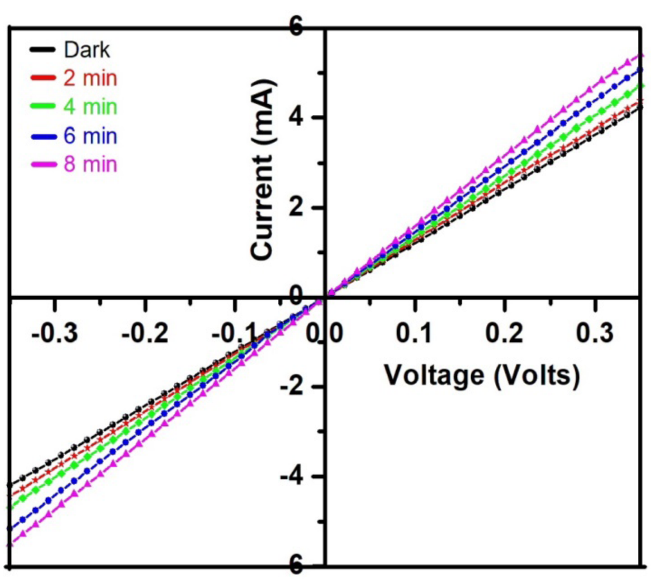

Figure 6: Typical I-V characteristics of Ag/CdSe/Ag M-S-M structure, under dark and visible-light irradiation

I-V characteristics indicates that the material's resistivity has decreased continuously with visible light illumination. This indicates that the free electron-hole pairs are available for current conduction within the material.[33] The dark resistivity is found to be 0.8310^{2} Ω.cm, and it decreases to 0.6410^{2} Ω.cm for nanocrystalline CdSe after illumination of visible light.

Figure 7 shows the I-V curve of the CdSe visible-light photoconductive detector's net photocurrent by subtracting dark current from the measured current, under visible light illumination with Ag as contact electrode.[35] It is seen that under 0.25-volt bias, CdSe thin film shows net photocurrent of the order of 37.1, 37.4, 65.4, and 95.1 mA corresponding to the illumination of visible-light for 2, 4, 6, and 8 minuted, respectively. This show that even at low bias voltage, number of electron could pass metal-semiconductor junction, which results in good visible-light photoresponse.[35] Figure 7 shows that for higher visible-light illumination time, the I-V photocurrent curve is almost linear, confirming the good ohmic contact of the photoconductive detector. Due to the good ohmic contact between CdSe thin film and Ag electrode, a large number of conductive paths are created in the film, which helps in the rapid transport of photoelectrons in CdSe thin film to Ag electrode.[35,36] (Figure 8)

Photosensitivity[33,37] is one of the significant property which defines the how well the photosensor is fabricated, which can be calculated by using the relation;

$$S = \frac{R_D - R_L}{R_D} \tag{1}$$

where R_D and R_L is the resistance in dark and under illumination, respectively.

Photoresponsitivity (R) is another important parameter for a photosensor, which is defined as the photocurrent generated per unit power of the incident light on the effective area of a photosensor and can be calculated by the equation,[38]

$$R = \frac{\Delta I}{PS} \tag{2}$$

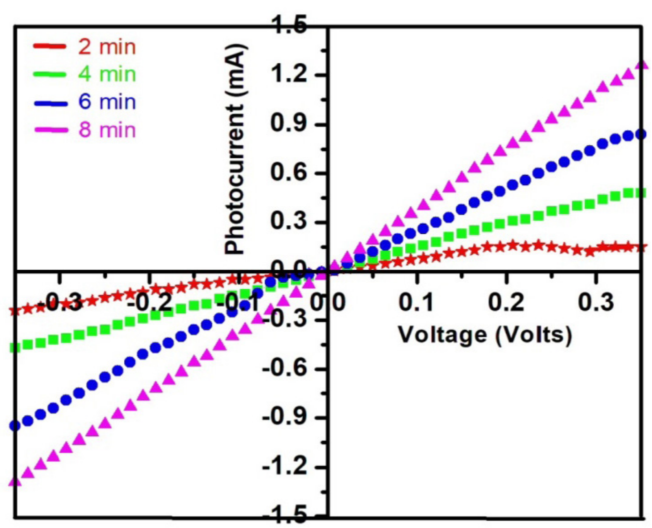

Figure 7: Plot of photocurrent versus voltage for Ag/CdSe/Ag M-S-M structure.

Where, ΔI be the photocurrent, P be the power of incident light, and A be the effective area of the photosensor. Figure 8 exhibits the photosensitivity and responsivity as a function of visible-light illumination time. The photosensitivity along with responsivity increases with visible-light illumination time. It can be concluded that the enhancement of the photoconductive sensitivity is due to the electron-hole pairs excited by the incident light.[39] These results indicate that the fabricated photodetector demonstrates sensitivity towards the visible-light.

I-V Characterization of Ag/CdSe/ITO Schottky contact

In order to investigate the diode characteristics of Ag/CdSe Schottky contact, I-V measurement is carried out at room temperature under dark condition as well as illumination with visible-light and typical device configuration is shown in Figures 3 and 9 shows the typical I-V curves of Ag/CdSe Schottky diode under the dark condition as well as illumination with visible-light. The device's I-V curve exhibited a typical rectifying behavior, proving that the fabricated Ag/CdSe heterojunction is a Schottky junction with a forward threshold voltage of 0.37 volt. The rectification ratio, which is the ratio of forward current to reverse current at certain voltage, is one of the important parameter of the Schottky diode. The rectification ratio of the prepared Schottky contact was found to be 1.17, which is quite comparable to the value of rectification ratio reported for aluminium/5,14-dihydro-5,5,12,14-tetraazopentacenes doped Schottky barrier contact.[40] This result confirmed that the soft chemical solution method can fabricate Ag/CdSe Schottky contact on ITO.

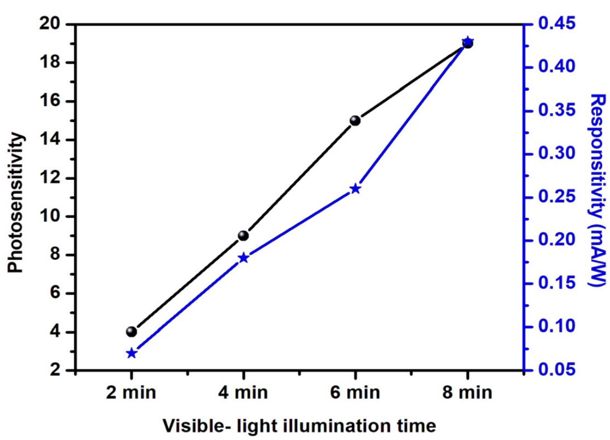

Figure 8: Plot of photosensitivity and responsivity as a function of visible-light illumination time.

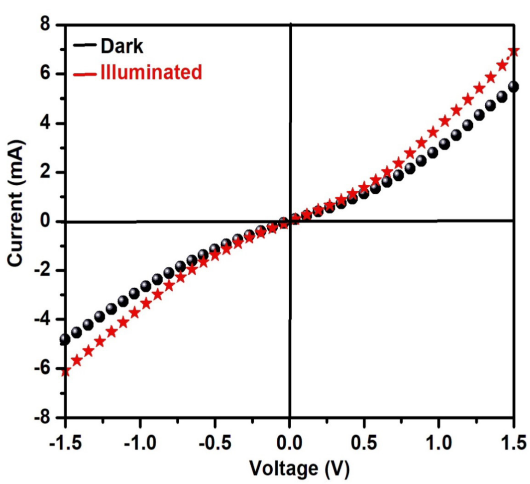

Figure 9: Typical I-V curves of Ag/CdSe Schottky diode under dark and visible-light illumination.

In order to evaluate the feasibility of the fabricated Schottky contact, as visible-light photodetector, I-V measurement is conducted under the illumination of visible-light and result is shown in Figure 9. Comparison with the dark current, the photocurrent upon exposure to visible-light increases significantly. This is attributed to the generation of vast excited electron-hole pairs, which increases the current [39]. This behavior is consistent with an increase in the number of free carriers in the semiconductor under illumination.[41] As discussed earlier, responsitivity (R) is considered as one of the important parameters of an optoelectronic device and calculated R value of the fabricated device was found to be 0.81 mA/W. Our device's responsivity was comparable to the previously reported Pt/Cr doped ZnO/Pt Schottky diode under visible-light.[1] Since the present study is about to test the photosensing property exhibited by low-cost visible-light photodetector based on Ag/CdSe Schottky diode, the optical characteristics such as sensitivity, gain and photoresponse were not examined.

Conclusion

In conclusion, visible-light photodetector based on Ag/CdSe Schottky diode was fabricated by a simple, low cost and low-temperature soft chemical solution method. X-ray diffraction pattern of CdSe films indicates a nanocrystalline structure with a hexagonal system. Surface morphology using FESEM indicates uniform distribution of spherical grains of different sizes on the ITO surface. The I-V characteristics of Ag/CdSe/Ag metal-semiconductor-metal structure confirm the ohmic nature of the fabricated device and it exhibited a good photosensitivity and photo-responsivity under the illumination of visible-light. The formation of Ag/CdSe Schottky diode was also realized by observing rectifying junction between CdSe and Ag electrode. The forward threshold voltage of Ag/CdSe Schottky diode was found to be 0.37 volt. The significant increase in the current both at forward and reverse direction under light irradiation, indicating that Ag/CdSe Schottky diode functions as a visible-light photodetector. Thus, this work demonstrates that the photodetector based on Ag/CdSe Schottky diode has great potential opportunities for future optoelectronic device applications.

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