FABRICATION OF THE P-N JUNCTION ULTRAVIOLET PHOTODETECTORS BASED ON METAL OXIDE NANOPARTICLES

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ABSTRACT: Recently, wide bandgap metal oxides have attracted tremendous attention in the field of UV photodetectors due to their promising optoelectronic properties. Up to now, various approaches have been used to design metal oxide-based UV photodetectors. Among these designs, p-n junction UV photodetectors exhibited remarkable performance. In this study, TiO$_2$/CuCrO$_2$ p-n junction as a UV photodetector was fabricated with spin coating method for the first time. The morphological and optical properties of the fabricated devices were investigated in detail. Moreover, the effect of the CuCrO$_2$ thickness on the performance of the UV photodetector was explored. The fabricated devices showed promising diode behavior and UV response. The responsivity ($R$) and specific detectivity ($D^*$) of the best device were 3.11 mA/W and 2.37x10$^{11}$ Jones, respectively at -1.5 V under 3 mW/cm$^2$ light intensity.

Keywords: UV photodetector, Metal oxide nanoparticles, P-N heterojunction, Thin film

1. INTRODUCTION

The Ultraviolet (UV) photodetectors, which convert the UV light energy into electric signals, find many applications such as light-wave communications, flame detection, ozone monitoring, and missile detection (Zou et al., 2018). Traditionally, a photomultiplier tube (PMT) and silicon have been used as UV photodetectors; however, high voltage and vacuum environment requirement of PMTs and the necessity of using optical filters to block visible and infrared part of the electromagnetic spectrum for silicon-based UV photodetectors have created the need for the development of new UV photodetector materials (Xie et
al., 2019). Due to their wide bandgap, metal oxides such as Ga₂O₃, ZnO, SnO₂, and TiO₂ have attracted considerable attention as alternative materials for UV photodetectors (Deka Boruah, 2019; Wu and Kuo, 2009; Xu et al., 2019; Yadav et al., 2022). Among these materials, TiO₂ is one of the most extensively researched n-type semiconductor materials due to its radiation hardness, thermal and chemical stability, easy and low-cost fabrication, and promising optical and electrical properties (Noman et al., 2019). Up to now, various device designs have been developed to fabricate efficient TiO₂-based photodetectors (Huang et al., 2011; Karaagac et al., 2012; Li et al., 2012; Nicolaescu et al., 2021). Fabricating the heterojunction device with TiO₂ and p-type semiconductor is one of the effective techniques for enhancing the photogenerated charge separation efficiency, which improves the photodetector performance (Yang et al., 2021). Moreover, an inner electric field is created at the interface with the formation of the p-n heterojunction. Therefore, the photogenerated electron-hole pairs in the depletion regions are separated without an external power supply (Gao et al., 2018).

Many organic and inorganic p-type semiconductors have been applied as a p-type counterpart to fabricate TiO₂ based p-n junction UV photodetectors (Nicolaescu et al., 2021; Wang et al., 2015; Zheng et al., 2016). Due to the stability concern of organic semiconductors, inorganic p-type semiconductors, mainly metal oxides, come to the fore in p-n junction UV photodetectors. However, the poor conductivity of the p-type metal oxide semiconductors generally inhibits the efficient transport of the photogenerated carriers. Therefore, extensive research efforts have been put into developing the new p-type metal oxides.

The copper-based delafossite oxides (CuMO₂, M: Al, Cr, Ga, etc.) are promising p-type semiconductors with a wide bandgap (Zhang et al., 2019). Among these materials, CuCrO₂ (Eg ~3.1 eV) has shown the best optoelectronic properties and has been used in various areas such as transparent conducting oxides, transparent diodes, photocatalysis, gas sensors, and solar cells (Bai et al., 2021; Dursun et al., 2018; Kaya et al., 2018; Tonooka and Kikuchi, 2006; Zhou et al., 2009). There are also a few recently reported studies where CuCrO₂ has been used to fabricate p-n junction photodetectors such as ZnO/CuCrO₂, Al-doped ZnO / Mg, and N-doped CuCrO₂ and Ga₂O₃/CuCrO₂ (Ahmadi et al., 2021; Cossuet et al., 2018; Wu et al., 2021). All the photodetectors fabricated based on the CuCrO₂ showed significant diode behavior and high UV responsivity.

CuCrO₂ can also be considered potential p-type semiconductors for TiO₂ based p-n junction UV photodetectors due to their high p-type conductivity, wide bandgap, and type-II alignment with TiO₂. In this study, TiO₂/CuCrO₂ heterojunction films as a UV photodetector were fabricated using a simple solution-based method for the first time. The optical and morphological properties of the films and UV photodetector performances of the devices were studied.

2. MATERIALS AND METHOD

2.1. Fabrication of The P-N Heterojunction UV Photodetectors

In order to fabricate p-n heterojunction, TiO₂ and CuCrO₂ films were deposited on the fluorine-doped tin oxide (FTO) coated glass substrate by a spin coating method. FTO substrates were cleaned in an ultrasonic bath using de-ionized water, acetone, and ethanol for 15 minutes before the film deposition. After cleaning the substrates, diluted TiO₂ paste (30NRD, Dyesol, TiO₂/ethanol:1/6, w/w) was coated on the FTO layer at 4000 rpm for 20 s using spin coating and annealed at 450 °C for 30 min in air. Hydrothermally synthesized CuCrO₂ nanoparticles were used as a p-type counterpart of the p-n junction. Synthesized procedure and properties of the CuCrO₂ nanoparticles were explained in our previous studies in detail (Kaya et al., 2016). In order to form CuCrO₂ film on the TiO₂ layer, 5 mg/mL CuCrO₂ dispersion in isopropanol was spin-coated at 3000 rpm for 30 s and was annealed at 300 °C for one h. CuCrO₂ films with different thicknesses were produced to investigate the effect of the p-type layer thicknesses on the photodetector performance. CuCrO₂ thickness was adjusted by changing the number of the coatings layers (10 and 20 layers). Finally, a copper tape foil (4 x 4 mm) was used as an electrode on top of the p-n heterojunction.
2.2. Characterization

The transmittance spectra of the films were recorded between 300-800 nm using Shimadzu UV-2600 UV–Vis spectrophotometer. The microstructural features of the films were investigated using SM Zeiss LS-10 scanning electron microscope (SEM). The current density–voltage (J–V) curves of devices were recorded by Gamry Interface 1010B Potentiostat/Galvanostat. A 365 nm UV LED (Cree LED, 3W) was used as a light source. The power density of the incident light was adjusted by changing the distance between the UV LED and the sample. The illumination power was measured using a Newport 842-PE power meter equipped with a Newport 818P power detector.

3. RESULTS AND DISCUSSION

The morphological properties of both TiO$_2$ and CuCrO$_2$ films were examined by SEM analysis. SEM images of the TiO$_2$ film on the FTO layer, 10 layers of CuCrO$_2$ film, and 20 layers of CuCrO$_2$ film on the TiO$_2$ layer are presented in Figure 1 (a), (b), and (c), respectively. As can be seen from Figure 1(a), continuous TiO$_2$ nanoparticulate film deposited the whole FTO surface uniformly. Although the CuCrO$_2$ nanoparticles seemed to be largely deposited individually throughout the film, some CuCrO$_2$ nanoparticles agglomerated and were not distributed (Figure 1(b) and (c)). Moreover, small pinholes were observed on the surface of the CuCrO$_2$ films. The formation of the pinholes is a sign of poor coverage of the TiO$_2$ film surface, which can result in direct contact between the TiO$_2$ layer and the metal electrode.

![Figure 1. SEM images of the (a) TiO$_2$, (b) 10 layers of CuCrO$_2$ film, and (c) 20 layers of CuCrO$_2$ film (The SEM images were captured at 100 kx magnification)](image)

The optical properties of the TiO$_2$ film and TiO$_2$/CuCrO$_2$ p-n junctions were investigated by measuring the absorbance and transmittance spectra in the wavelength range 300-800 nm with a UV–VIS spectrophotometer. The transmittance and absorbance spectra of the FTO, FTO/TiO$_2$, FTO/TiO$_2$/10 layers CuCrO$_2$, and FTO/TiO$_2$/20 layers CuCrO$_2$ are given in Figure 2 (a) and (b), respectively. The transmittance value of the FTO substrate was ~80% in the visible range (400–700 nm) of the electromagnetic spectrum. It is important to note that the TiO$_2$ film slightly improved the optical transmittance of the FTO layer between the 380 and 500 nm wavelength. It can be attributed to the formation of the smoother surface when the FTO layer is covered with TiO$_2$ film. On the other hand, deposition of the 10 layers of CuCrO$_2$ film on the TiO$_2$ layer surface decreased the transmittance of the device. The transmittance value of the p-n junction fabricated with 10 layers of CuCrO$_2$ was ~40%. Therefore, the p-n junction with 10 layers of CuCrO$_2$ can be called a semi-transparent device. However, further increasing the thickness of the CuCrO$_2$ layer (20 layers) led to a decrease in transmittance value to ~20% in the visible range, which can be explained by a high light-scattering due to the porous and rough film (Ko et al., 2012). In addition, the absorbance spectra are shown in Figure 2(b) revealed that all the samples exhibited strong absorption in the UV region. However, the absorption edges of the samples were different from each other. The absorption edge of the FTO, FTO/TiO$_2$, FTO/TiO$_2$/10 layers CuCrO$_2$, and FTO/TiO$_2$/20 layers CuCrO$_2$ were found to be ~325 nm,
335 nm, 351 nm, and 402 nm, respectively. Therefore, the devices fabricated with 20 layers of CuCrO$_2$ would absorb all the UV-A regions.

The device configuration for the p-n heterojunction photodetectors fabricated in this study was FTO/TiO$_2$/CuCrO$_2$/Cu, as shown in a schematic illustration in Figure 3(a). While the thickness of the TiO$_2$ was held constant, two different thicknesses of CuCrO$_2$ were coated by adjusting the number of coating layers (10 and 20 layers). Thus, the effect of the CuCrO$_2$ thickness on the photodetector performance of the p-n heterojunction was explored. All the photodetectors were illuminated through the glass substrate side during the current-voltage (I-V) measurements. The dark and 365 nm UV light illuminated J-V curves of the p-n heterojunctions fabricated with CuCrO$_2$ with 10 and 20 layers are given in Figure 3(b) and (c), respectively. In dark conditions, the current density under reverse bias was lower than that of the under forward bias for all the devices, resulting in non-linear J-V curves. This situation suggests that all the fabricated devices behave like rectifiers which proves the formation of a p-n junction diode. The $J_{\text{forward}}/J_{\text{reverse}}$ ratios (rectification ratio) at 1.5 V were 1.57 and 13.54 for the TiO$_2$/CuCrO$_2$ p-n junctions fabricated with 10 and 20 layers of CuCrO$_2$, respectively. The low rectification ratio of the device fabricated with thin CuCrO$_2$ (10 layers) can be attributed to the poor surface coverage of the CuCrO$_2$ film on the TiO$_2$ surface. As can be seen in the figures, at both reverse and forward bias voltages, the current density of the devices increased under the 365 nm UV light illumination. Moreover, the photocurrent value of both devices increased with increasing light intensity, which showed that the devices are photosensitive to UV light with 365 nm wavelength and generate the photocurrent. It is worth noting that although the formation of the p-n junction, the current density of the devices was almost zero under UV illumination in zero bias voltage. It can be due to the high defect density at TiO$_2$/CuCrO$_2$ heterojunction interface due to the void formation between nanoparticulate-based films. Therefore, the photogenerated carriers cannot be transferred without a bias voltage.
The responsivity can be defined as the photogenerated current per unit incident light power (Deka Boruah, 2019). Therefore, it is one of the critical parameters to determine the performance of the photodetector. The responsivity values of the detectors were calculated according to the following equation:

$$R = \frac{I_{\text{light}} - I_{\text{dark}}}{P_i}$$  \hspace{1cm} (1)

Where $R$ is the responsivity and $P_i$ is the incident light power. The responsivity values of the p-n heterojunctions fabricated with 10 and 20 layers of CuCrO$_2$ are shown in Fig 4(a) and 4(b), respectively. As can be seen in the figures, the responsivity values of the detectors were calculated at -1 and -1.5 V under four different UV power densities at 365 nm to investigate the effect of applied bias voltage and the light intensity. The responsivity value of the detector with 10 layers of CuCrO$_2$ was 0.10 mA/W at -1V under 3 mW/cm$^2$ light intensity and enhanced to 0.25 mA/W with increasing voltage (-1.5 V) due to the effective separation of the electron-hole pairs with a driving force of the bias voltage.
Figure 4. Responsivity and detectivity of the UV photodetectors fabricated with (a) 10 layers of CuCrO$_2$ film, (b) 20 layers of CuCrO$_2$ film for a UV illumination of 3, 6, 13, and 18 mW/cm$^2$ at an applied bias of -1 V and -1.5 V.

The responsivity value was further improved to 1.18 mA/W at -1 V under 3 mW/cm$^2$ light intensity by increasing the CuCrO$_2$ film thickness due to the formation of the continuous CuCrO$_2$ film. When the applied bias voltage was increased to -1.5 V, the responsivity value reached 3.11 mA/W under 3 mW/cm$^2$ light intensity. As mentioned before, the photocurrent value of the detector increased with increasing the light intensity due to the generation of more electron-hole pairs. However, the formation of more electron-hole pairs increases the charge carrier scattering and recombination probability which adversely affects the responsivity of the detector. Therefore, the responsivity value of both detectors decreased with increasing light intensity.

Table 1. Photodetector performances of the p-n junction heterojunctions involving CuCrO$_2$ as the p-type layer

| Materials           | Light source (nm) | Light intensity (mW/cm$^2$) | Responsivity (mA/W) | Specific detectivity (Jones) | References                  |
|---------------------|-------------------|----------------------------|----------------------|------------------------------|-----------------------------|
| ZnO/CuCrO$_2$       | 365               | 0.2                        | 3.43 (zero bias)     | 8.5x10$^9$ (-1V)             | (Cossuet et al., 2018)     |
| ZnO:Al/CuCrO$_2$:Mg, N | 385               | 0.2-1.2                    | 1.645 (1 V)          | 3.5x10$^{12}$ (1 V)            | (Ahmadi et al., 2021)     |
| Ga$_2$O$_3$/CuCrO$_2$ | 365               | 50 µW/cm$^2$               | 0.12 (zero bias)     | 4.6x10$^{11}$ (-1 V)          | (Wu et al., 2021)         |
| TiO$_2$/CuCrO$_2$   | 365               | 3                         | 1.18 (-1 V)          | 5.54x10$^{10}$ (-1 V)         | In this study              |
| TiO$_2$/CuCrO$_2$   | 365               | 3                         | 3.11 (-1.5 V)        | 2.37x10$^{11}$ (-1.5 V)       | In this study              |
Another crucial parameter for the photodetectors is the detectivity which can be defined as the weak signals detection ability from the noise environment (Deka Boruah, 2019). The specific detectivity values of the detectors were calculated according to the following equation:

\[
D^* = \frac{R}{\sqrt{2qJ_{dark}}}
\]

Where \(D^*\) is the specific detectivity (typically quoted in Jones, cm Hz\(^{1/2}\)/W), \(R\) is the responsivity (mA/W), \(q\) is the elementary charge (1.602x10\(^{-19}\) C), \(J_{dark}\) is the dark current, respectively. The specific detectivity value is used to determine the sensitivity of the device. Similar to the responsivity results, the device fabricated with 20 layers of CuCrO\(_2\) exhibited maximum specific detectivity of 2.37x10\(^{11}\) jones at -1.5 V under 3 mW/cm\(^2\) light intensity. This result revealed that the device with 20 layers of CuCrO\(_2\), which exhibited the highest responsivity, was also more sensitive than the device fabricated with 10 layers of CuCrO\(_2\). Comparisons between the device in this work and some reported p-n junction heterojunctions involving CuCrO\(_2\) as the p-type layer are listed in Table 1. As can be seen in the Table, various experimental parameters such as light source, light intensity, and bias voltage affect the performance of the device. It is still worth to mention that the photodetector performance of the TiO\(_2\)/CuCrO\(_2\) p-n junction presented in this study is promising and can be further developed to fabricate self-powered p-n junction photodetectors.

4. CONCLUSION

In summary, the TiO\(_2\)/CuCrO\(_2\) p-n junction was fabricated on the FTO layer using a simple spin coating method. The CuCrO\(_2\) film with two different thicknesses was successfully prepared on the TiO\(_2\) layer. The optical absorption of the TiO\(_2\)/CuCrO\(_2\) samples was strong in the UV region. On the other hand, the transmission in the visible region decreased with increasing the thickness of the CuCrO\(_2\) layer. All the fabricated p-n junction devices behaved like rectifiers, proving the p-n junction formation. Although the formation of the p-n junction, the photocurrent of the device was almost zero under UV illumination in zero bias voltage due to the high defect density at TiO\(_2\)/CuCrO\(_2\) heterojunction interface. However, the devices generated the photocurrent under the UV light with 365 nm wavelength when the bias voltage was applied. The device fabricated with 20 layers of CuCrO\(_2\) showed higher responsivity and specific detectivity values than the device fabricated with 10 layers of CuCrO\(_2\) which can be attributed to the better surface coverage of 20 layers of CuCrO\(_2\) on the surface of the TiO\(_2\) film. The best performing device with the responsivity of 3.11 mA/W and specific detectivity of 2.37x10\(^{11}\) Jones, at -1.5 V under 3 mW/cm\(^2\) light intensity, was fabricated with 20 layers of CuCrO\(_2\). The results mentioned above revealed that the delafossite oxides such as CuCrO\(_2\) are attractive p-type semiconductors for developing the p-n junction UV photodetectors. Future research directions could include development of the TiO\(_2\)/CuCrO\(_2\) p-n junctions with continous films to obtain self-powered UV photodetectors.

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REFERENCES

Ahmadi, M., Abrari, M., Ghanaatshoar, M., 2021, "An all-sputtered photovoltaic ultraviolet photodetector based on co-doped CuCrO\(_2\) and Al-doped ZnO heterojunction", Sci Rep, 11, 18694.

Bai, Z., Chen, S.-C., Lin, S.-S., Shi, Q., Lu, Y.-B., Song, S.-M., et al., 2021, "Review in optoelectronic properties of p-type CuCrO\(_2\) transparent conductive films", Surfaces and Interfaces, 22, 100824.
Cossuet, T., Resende, J., Rapenne, L., Chaix-Pluchery, O., Jiménez, C., Renou, G., et al., 2018, "ZnO/CuCrO₂ core-shell nanowire heterostructures for self-powered UV photodetectors with fast response", Advanced Functional Materials, 28.

Deka Boruah, B., 2019, "Zinc oxide ultraviolet photodetectors: rapid progress from conventional to self-powered photodetectors", Nanoscale Advances, 1, 2059-2085.

Dursun, S., Kaya, I. C., Kalem, V., Akyildiz, H., 2018, "UV/visible light active CuCrO₂ nanoparticle–SnO₂ nanofiber p-n heterostructured photocatalysts for photocatalytic applications", Dalton Transactions, 47, 14662-14678.

Gao, Y., Xu, J., Shi, S., Dong, H., Cheng, Y., Wei, C., et al., 2018, "TiO₂ nanorod arrays based self-powered UV photodetector: heterojunction with NiO nanoflakes and enhanced UV photoresponse", ACS Applied Materials & Interfaces, 10, 11269-11279.

Huang, H., Xie, Y., Yang, W., Zhang, F., Cai, J., Wu, Z., 2011, "Low-Dark-Current TiO₂ MSM UV Photodetectors With Pt Schottky Contacts", IEEE Electron Device Letters, 32, 530-532.

Karaagac, H., Erdal Aygun, L., Parlak, M., Ghaffari, M., Biyikli, N., Kemal Okyay, A., 2012, "Au/TiO₂ nanorod-based Schottky-type UV photodetectors", physica status solidi (RRL) – Rapid Research Letters, 6, 442-444.

Kaya, I. C., Akin, S., Akyildiz, H., Sonmezoglu, S., 2018, "Highly efficient tandem photoelectrochemical solar cells using coumarin6 dye-sensitized CuCrO₂ delafossite oxide as photocathode", Solar Energy, 169, 196-205.

Kaya, I. C., Sevindik, M. A., Akyildiz, H., 2016, "Characteristics of Fe- and Mg-doped CuCrO₂ nanocrystals prepared by hydrothermal synthesis", Journal of Materials Science: Materials in Electronics, 27, 2404-2411.

Ko, Y. H., Raju, G. S. R., Kim, S., Yu, J. S., 2012, "Diffuse light-scattering properties of nanocracked and porous MoO₃ films self-formed by electrodeposition and thermal annealing", physica status solidi (a), 209, 2161-2166.

Li, X., Gao, C., Duan, H., Lu, B., Pan, X., Xie, E., 2012, "Nanocrystalline TiO₂ film based photoelectrochemical cell as self-powered UV-photodetector", Nano Energy, 1, 640-645.

Nicolaescu, M., Bandas, C., Orha, C., Şerban, V., Lazâu, C., Căprârescu, S., 2021, "Fabrication of a UV photodetector based on n-TiO₂/p-CuMnO₂ heterostructures", Coatings, 11, 1380.

Noman, M. T., Ashraf, M. A., Ali, A., 2019, "Synthesis and applications of nano-TiO₂: a review", Environmental Science and Pollution Research, 26, 3262-3291.

Tonooka, K., Kikuchi, N., 2006, "Preparation of transparent CuCrO₂:Mg/ZnO p–n junctions by pulsed laser deposition", Thin Solid Films, 515, 2415-2418.

Wang, H., Yi, G., Zu, X., Jiang, X., Zhang, Z., Luo, H., 2015, "A highly sensitive and self-powered ultraviolet photodetector composed of titanium dioxide nanorods and polyaniline nanowires", Materials Letters, 138, 204-207.

Wu, C., Qiu, L., Li, S., Guo, D., Li, P., Wang, S., et al., 2021, "High sensitive and stable self-powered solar-blind photodetector based on solution-processed all inorganic CuMnO₃/Ga₂O₃ pn heterojunction", Materials Today Physics, 17, 100335.

Wu, J.-M., Kuo, C.-H., 2009, "Ultraviolet photodetectors made from SnO₂ nanowires", Thin Solid Films, 517, 3870-3873.

Xie, C., Lu, X.-T., Tong, X.-W., Zhang, Z.-X., Liang, F.-X., Liang, L., et al., 2019, "Recent progress in solar-blind deep-ultraviolet photodetectors based on inorganic ultrawide bandgap semiconductors", Advanced Functional Materials, 29.

Xu, J., Zheng, W., Huang, F., 2019, "Gallium oxide solar-blind ultraviolet photodetectors: a review", Journal of Materials Chemistry C, 7, 8753-8770.

Yadav, P. V. K., Ajitha, B., Ahmed, C. M. A., Reddy, Y. A. K., Minnam Reddy, V. R., 2022, "Superior UV photodetector performance of TiO₂ films using Nb doping", Journal of Physics and Chemistry of Solids, 160, 110350.
Yang, D., Du, F., Ren, Y., Kang, T., Hu, P., Teng, F., et al., 2021, "A high-performance NiO/TiO₂ UV photodetector: the influence of the NiO layer position", Journal of Materials Chemistry C, 9, 14146-14153.

Zhang, N., Sun, J., Gong, H., 2019, "Transparent p-type semiconductors: copper-based oxides and oxycalcogenides", Coatings, 9, 137.

Zheng, L., Teng, F., Zhang, Z., Zhao, B., Fang, X., 2016, "Large scale, highly efficient and self-powered UV photodetectors enabled by all-solid-state n-TiO₂ nanowell/p-NiO mesoporous nanosheet heterojunctions", Journal of Materials Chemistry C, 4, 10032-10039.

Zhou, S., Fang, X., Deng, Z., Li, D., Dong, W., Tao, R., et al., 2009, "Room temperature ozone sensing properties of p-type CuCrO₂ nanocrystals", Sensors and Actuators B: Chemical, 143, 119-123.

Zou, Y., Zhang, Y., Hu, Y., Gu, H., 2018, "Ultraviolet detectors based on wide bandgap semiconductor nanowire: A review", Sensors (Basel), 18.