Preparation of Cu$_3$N/MoS$_2$ Heterojunction through Magnetron Sputtering and Investigation of Its Structure and Optical Performance

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Received: 25 March 2020; Accepted: 13 April 2020; Published: 16 April 2020

Abstract: Cu$_3$N/MoS$_2$ heterojunction was prepared through magnetron sputtering, and its optical band gap was investigated. Results showed that the prepared Cu$_3$N/MoS$_2$ heterojunction had a clear surface heterojunction structure, uniform surface grains, and no evident cracks. The optical band gap (1.98 eV) of Cu$_3$N/MoS$_2$ heterojunction was obtained by analyzing the ultraviolet-visible transmission spectrum. The valence and conduction band offsets of Cu$_3$N/MoS$_2$ heterojunction were 1.42 and 0.82 eV, respectively. The Cu$_3$N film and multilayer MoS$_2$ formed a type-II heterojunction. After the two materials adhered to form the heterojunction, the interface electrons flowed from MoS$_2$ to Cu$_3$N because the latter had higher Fermi level than the former. This behavior caused the formation of additional electrons in the Cu$_3$N and MoS$_2$ layers and the change in optical band gap, which was conducive to the charge separation of electrons in MoS$_2$ or MoS$_2$ holes. The prepared Cu$_3$N/MoS$_2$ heterojunction has potential application in various high-performance photoelectric devices, such as photocatalysts and photodetectors.

Keywords: Cu$_3$N/MoS$_2$ films; heterojunction; magnetron sputtering; photocatalysis

1. Introduction

Environmental problems have worsened due to the rapid consumption of fossil fuels. Thus, efficient, energy-saving, and environmentally friendly methods must be developed to solve various pollution problems [1]. Among them, photocatalysis is a widely used technology in solar energy conversion and shows good potential [2,3]. Other available methods are sewage treatment [4,5] and dye degradation [6,7]. Heterojunctions formed with 2D materials and other semiconductors have recently attracted attention from researchers due to their various potential applications. Many heterojunction materials, including semiconductors/semiconductors, metals/semiconductors, molecules/semiconductors [8,9], and multiple heterojunctions [10], have been used in photocatalysis and achieved considerable success. Heterojunction photocatalysts typically have the following advantages: strong light absorption [11], efficient charge separation and transport [12], cocatalyst effect, and strong light absorption stability [13].

Among these heterojunctions, Cu$_3$N/MoS$_2$ shows promise as a photocatalyst because Cu$_3$N is an outstanding semiconductor material that can substantially enhance the photoelectric performance of MoS$_2$ or introduce new functions into such heterojunctions. As a typical transition metal sulfide, MoS$_2$ has a S–Mo–S sandwich structure combined by the van der Waals force [14,15]. Given its unique structure and photoelectric properties, MoS$_2$ has attracted considerable attention from scholars [16,17] and has been widely investigated for thin film transistors [18,19], photodetectors [20,21], and solid lubrication [22,23]. Owing to its adjustable band gap, MoS$_2$ can be combined with
many types of semiconductors to enhance light absorption from the ultraviolet to visible light regions [7,24], increase the separation and lifetime of charge carriers, and provide potential applications in visible-light catalysis [25,26]. Cu$_3$N is a widely used material because of its metal-to-semiconductor properties [27,28]. Cu$_3$N has been proposed for battery materials [2,29], catalyst additives [30], spin tunnel junction [31], memory [32], and electric transport materials [33] due to its wide range of optical band gap, low temperature of thermal decomposition, and excellent chemical activity.

Heterojunctions, such as MoS$_2$/ZnO [13], MoS$_2$/TiO$_2$ [11], and TiO$_2$/WO$_3$ [34], remarkably improve the electrical conductivity and optical properties of materials. However, to the best of our knowledge, Cu$_3$N/MoS$_2$ heterojunction materials have not been investigated. In addition, the complicated and limited preparation of most heterogeneous structures usually involves many steps and thus is not conducive to large-scale operations. Therefore, a simple and effective preparation method for Cu$_3$N/MoS$_2$ heterojunction is needed. Magnetron sputtering has become a popular technique due to its advantages of fast deposition speed, wide target range, good sample quality, and controllable parameters.

Our previous work investigated the photocatalytic properties of Cu$_3$N/MoS$_2$ composite films. In contrast, in this study, we made a more detailed and accurate study of the Cu$_3$N/MoS$_2$ heterojunction, and explained in more depth the reasons for the change in the band gap of the Cu$_3$N/MoS$_2$ heterojunction. Through the corresponding calculation, we found that the Cu$_3$N/MoS$_2$ heterojunction has better optical performance. In this study, Cu$_3$N/MoS$_2$ heterojunction was fabricated through magnetron sputtering, and its crystal structure, chemical composition, surface morphology, and band gap structure were explored.

2. Experimental

Cu$_3$N/MoS$_2$ heterojunctions were prepared on single-crystal silicon (100) and quartz substrates by using RF magnetron sputtering (JGP-450a, SKY Technology Development Co., Ltd, Shenyang, China). First, the silicon and quartz wafer substrates were separately sonicated in an acetone and ethanol solution for 15 min, rinsed with deionized water, and dried for further use. Second, the processed monocrystalline silicon and quartz wafers were placed in the substrate support, the target was installed, and the sputtering chamber was closed. Third, the sputtering chamber was evacuated to 2.5 Pa with a mechanical pump and the vacuum was driven to $1 \times 10^{-4}$ Pa by using a turbomolecular pump. Before the experiment, the target was presputtered in Ar atmosphere for 10 min and the surface of the target was cleaned to remove the oxide. Fourth, the MoS$_2$ layer was deposited on the substrate using high-purity molybdenum disulfide target (99.99%, Beijing Jingmai Zhongke Material Technology Co., Ltd., Beijing, China) in Ar atmosphere at room temperature. Total gas flow rate, vacuum chamber pressure, power, and sputtering time were set to 40 sccm, 1.0 Pa, 150 w, and 2 and 3.5 min, respectively. Fifth, a Cu$_3$N layer was deposited on the MoS$_2$ layer with a sputtering time of 2 min using a copper target (99.99%, Beijing Jingmai Zhongke Material Technology Co., Ltd., Beijing, China). Total gas flow rate, flow ratio of N$_2$ and Ar, vacuum chamber pressure, power, and sputtering time were set to 40 sccm, 3:1, 1 Pa, 150 W, and 1.5 min, respectively. Under the same experimental conditions, a pure Cu$_3$N layer was deposited on the blank substrate for 3.5 min. The deposition rates of MoS$_2$ and Cu$_3$N layers are 12 and 13.3 nm/min, respectively. The diameter of molybdenum disulfide target and copper target are both 60 mm. The sputtering time for the heterojunction in the scanning electron microscopy (SEM, Hitachi, Tokyo, Japan) was enlarged 10 times, and the rest of the conditions remained unchanged to easily observe the heterojunction structure.

The surface morphology of heterojunction was characterized with a field emission scanning electron microscope (S-4800, Hitachi, Tokyo, Japan). The crystal structure of heterojunction was characterized using X-ray diffractometry (XRD, X’Pert PRO, PANalytical, Holland). Elemental characterization was conducted via X-ray photoelectron spectroscopy (XPS, Escalab, Thermo Fisher Scientific, MA, USA). The optical band gap of heterojunction was investigated with an ultraviolet-visible (UV-vis) spectrometer (UV-2600/2700, Shimadzu, Kyoto, Japan).
3. Results and Discussion

The XRD test patterns of MoS$_2$, Cu$_3$N, and Cu$_3$N/MoS$_2$ heterojunction are shown in Figure 1. The $2\theta$ in the MoS$_2$ (002), (100), (101), and (110) crystal planes was found at $14.55^\circ$, $32.3^\circ$, $36.5^\circ$, and $49.4^\circ$, respectively [22,35]. The absence of other impurity peaks in the spectrum indicated the high purity of the obtained MoS$_2$. Moreover, the sharp diffraction peak of MoS$_2$ revealed the good crystallinity of MoS$_2$. The average grain size of the heterojunction was 14.9 nm, which was smaller than the grain size observed in the SEM image. This may have been because the size of the grain aggregate observed by the SEM was not the size of the single grain; therefore, the particle size value observed by SEM was often larger than the calculated value. When the Cu$_3$N layer was deposited on the MoS$_2$ layer to form the Cu$_3$N/MoS$_2$ heterojunction, the sample still showed reflection on the (100), (101), and (110) crystal planes of MoS$_2$. However, the intensity of the (100), (101), and (110) crystal planes of MoS$_2$ in the Cu$_3$N/MoS$_2$ heterojunction was weaker than that in the pure MoS$_2$ layer, indicating the reduced crystal quality of the MoS$_2$ layer after Cu$_3$N deposition. Compared with that of the pure Cu$_3$N layer, the strength of the (100) and (200) crystal planes of Cu$_3$N in the Cu$_3$N/MoS$_2$ heterojunction decreased, possibly due to the interdiffusion of atoms that occurred at the interface between MoS$_2$ and Cu$_3$N and led to the reduced quality of heterogeneous crystals.

![Figure 1](image1.png)

Figure 1. XRD patterns of the MoS$_2$ layer, Cu$_3$N layer, and Cu$_3$N/MoS$_2$ heterojunction.

The surface and cross-sectional morphology of the Cu$_3$N/MoS$_2$ heterojunction are shown in Figure 2. This surface of the MoS$_2$ layer was generally smooth and flat with block particles of uniform size and no evident cracks. These characteristics were beneficial to the growth of the Cu$_3$N layer on the surface of the MoS$_2$ layer. Figure 2b shows the thickness of the heterojunction. The MoS$_2$ and Cu$_3$N layers had a thicknesses of approximately 300 and 200 nm, respectively. The boundary between the layers clearly showed the heterojunction structure. The relationship between the film deposition thickness and deposition time suggested that the Cu$_3$N/MoS$_2$ heterojunction was approximately 50 nm-thick.
The distribution of elements in the Cu₃N/MoS₂ heterojunction and the atomic percentage of each element are shown in Figure 3. EDS data revealed that the ratio of Cu to N atoms in the heterojunction was around 1. Moreover, its chemical ratio differed from the standard ratio of Cu₃N, possibly because of the free Cu atoms in the heterojunction. These free atoms did not combine with the N atoms to form Cu₃N. However, fewer Mo and S atoms were detected on the surface of the heterojunction. The ratio of Mo and S atoms was about 1.87. This phenomenon occurred because MoS₂ can be found in the lower layer, and some Mo atoms in the lower layer had moved to the surface. Meanwhile, the S atoms had difficulty in reaching the surface. The atomic ratio of Cu and N in the film Cu₃N was 1:1, which does not meet the standard atomic ratio of Cu₃N, in which the N element was significantly more than the Cu element. This is because during the deposition process, the ratio of N₂ to Ar was high, and a part of the free N atoms were adsorbed between the crystal grains. However, when Mo: S = 3.11:1.66 = 1:0.53 ≈ 1.87:1, there were fewer S atoms. This may have been because when MoS₂ is deposited, a part of S becomes a single substance to escape, resulting in fewer S atoms. Mo atoms that were not combined into MoS₂ combined with MoO₃ to oxygen (as shown in Figure 4e,f). In addition, the XPS spectrum also proved that there were a large number of Cu⁺, N⁻ (as shown in Figure 4c,d), and Mo-S bonds (as shown in Figure 4e,f) in the film. It showed that the heterojunction is mainly composed of Cu₃N and MoS₂, and contains only a small amount of MoO₃ and N atoms, which does not affect the formation of Cu₃N/MoS₂ heterojunction. In addition, the Si atoms detected via EDS originated from the monocrystalline silicon substrate.

Figure 2. SEM image of Cu₃N/MoS₂ heterojunction deposited on silicon wafer: (a) surface of the MoS₂ layer and (b) cross-section of the heterojunction.

Figure 3. EDS spectrum of the Cu₃N/MoS₂ heterojunction.
Figure 4. XPS spectrum: (a) total spectrum of the Cu3N/MoS2 heterojunction, (b) MoS2 total spectrum, (c) Cu 2p peak fitting in the Cu3N/MoS2 heterojunction, (d) Cu 2p peak fitting in the Cu3N layer, (e) Mo 3d peak fitting in the Cu3N/MoS2 heterojunction, and (f) Mo 3d peak fitting in the MoS2 layer.

The chemical composition of the Cu3N/MoS2 heterojunction was characterized using XPS, and the test results are shown in Figure 4. Figure 4a,b illustrates the total spectrum of the Cu3N/MoS2 heterojunction and MoS2 thin film, respectively. Figure 4a depicts that the binding energies of the S2p, Mo 3d, N1s, O1s, and Cu2p peaks were 162.6, 227.8, 397.4, 530.5, and 931.3 eV, respectively [15]. Figure 4b shows that the S2p and Mo 3d peaks appeared at the binding energies of 161.5 and 229.5 eV, respectively. The O1s peak appearing in the spectrogram might be due to the inevitable atmospheric pollution in the heterojunction during transfer and testing. However, a weak S2p peak appeared at 162.6 eV possibly due to the trace S atoms sputtered out during the deposition of the remaining MoS2 layer in the vacuum chamber, thus causing pollution in the Cu3N layer. The high intensity peaks with binding energies of 931.1 and 952.1 eV correspond to the Cu2p3/2 and Cu2p1/2 peaks located at 933.9 and 952.6 eV, respectively [27]. In Figure 4c,d, weaker peaks appeared at the binding energies of 933.9, 952.6 eV, respectively. These peaks could be attributed to the S2s orbital and Mo–O hybrid bond structure that indicated the formation of Mo4+ in MoS2. The two weak peaks at 223.46 and 232.95 eV appeared at 162.6 eV possibly due to the trace S atoms sputtered out during the deposition of the remaining MoS2 layer in the vacuum chamber, thus causing pollution in the heterojunction during transfer and testing. However, a weak S2p peak could be attributed to the S2s orbital and Mo–O hybrid bond structure that indicated the formation of Mo4+ in MoS2. The two weak peaks at 223.46 and 232.95 eV could be inferred as the Mo3d3/2 orbital peak in the Mo–S hybrid bond structure in MoS2 that characterized Mo4+. The two main peaks located at 232.0 and 228.5 eV could be inferred as the Mo3d3/2 orbital peak in the Mo–S hybrid bond structure. The two main peaks located at 232.0 and 228.5 eV could be inferred as the Mo3d3/2 orbital peak in the Mo–S hybrid bond structure. The intensity peaks with binding energies of 933.9, 952.6 eV, respectively. These peaks could be attributed to the S2s orbital and Mo–O hybrid bond structure that indicated the formation of Mo4+ in MoS2. The two weak peaks at 223.46 and 232.95 eV could be inferred as the Mo3d3/2 orbital peak in the Mo–S hybrid bond structure. The intensity peaks with binding energies of 933.9, 952.6 eV, respectively. These peaks could be attributed to the S2s orbital and Mo–O hybrid bond structure that indicated the formation of Mo4+ in MoS2. The two weak peaks at 223.46 and 232.95 eV could be inferred as the Mo3d3/2 orbital peak in the Mo–S hybrid bond structure.
were 1.42 and 0.82 eV, respectively. The band gap values of MoS$_2$ were consistent with the XRD and EDS results and indicated a large number of MoS$_2$ peaks located at 232.0 and 228.5 eV could be inferred as the Mo3d$_{5/2}$ orbital peaks at the binding energies of 933.9 and 932.4 eV, respectively, as shown in Figure 4c. Figure 4d illustrates the fitting of Cu2p peaks in the Cu$_3$N layer with the Cu2p$_{3/2}$ and Cu2p$_{1/2}$ orbital peaks at the binding energies of 932.81 and 952.76 eV, respectively [27]. In Figure 4c,d, weaker peaks appeared at the binding energies of 933.9, 952.6 eV and 934.5, 954.4 eV, which belong to Cu$^{2+}$, which is caused by the slight oxidation of Cu$. Figure 4e,f depicts the Mo3d spectra in the Cu$_3$N/MoS$_2$ heterojunction and pure MoS$_2$ layers, respectively. After the XPS spectrum of Mo3d was fitted, four peaks appeared with different intensities. The two main peaks located at 232.0 and 228.5 eV could be inferred as the Mo3d$_{3/2}$ orbital peak in the Mo–S hybrid bond structure in MoS$_2$ that characterized Mo$^{4+}$ in MoS$_2$. The two weak peaks at 223.46 and 232.95 eV could be attributed to the S2s orbital and Mo–O hybrid bond structure that indicated the formation of sulfide and partial oxidation on the film surface [23]. However, the Mo–S hybrid bond of the Mo3d orbital peak of pure MoS$_2$ was located at the binding energies of 229.4 and 231.5 eV. The XPS spectra were consistent with the XRD and EDS results and indicated a large number of MoS$_2$ and Cu$_3$N in the heterojunction.

Figure 5 presents the energy band diagram of the Cu$_3$N/MoS$_2$ interface. The valence (VBO or $\Delta E_V$) and conduction (CBO or $\Delta E_C$) band offsets of the interface were calculated on the basis of the XPS spectra and corresponding band gap data as follows [13]:

$$\Delta E_V = (E_{Cu3N/MoS2}^{Val} - E_{MoS2}^{Val}) + (E_{MoS2}^{Mo3d_{5/2}} - E_{MoS2}^{VB}) - (E_{Cu3N}^{Mo3d_{5/2}} - E_{Cu3N}^{VB})$$  (1)

$$\Delta E_C = E_{g}^{Cu3N} - E_{g}^{MoS2} - \Delta E_V$$  (2)

where $E_m^s$ represents the energy of characteristic m in sample s, $E_{MoS2}^{Mo3d_{5/2}}$, $E_{Cu3N}^{Mo3d_{5/2}}$ denote the maximum valence band values of Mo3d$_{5/2}$ and Cu2p$_{3/2}$ in the MoS$_2$ and Cu$_3$N samples, respectively; and $E_{g}^{MoS2}$ and $E_{g}^{Cu3N}$ indicate the band gap values of the MoS$_2$ and Cu$_3$N samples, respectively.

![Figure 5. Band diagram of the Cu$_3$N/MoS$_2$ interface.](image)

According to Equations (1) and (2), the VBO and CBO between the MoS$_2$ and Cu$_3$N samples were 1.42 and 0.82 eV, respectively. The band gap values of MoS$_2$ and Cu$_3$N at 2.43 and 1.83 eV, respectively, were consistent with those measured in the US–vis transmission spectrum, and the maximum valence band values (VBM) of MoS$_2$ and Cu$_3$N were 1.15 and 1.40 eV, respectively [13]. The energy band diagram of the Cu$_3$N/MoS$_2$ heterojunction interface could be deduced on the basis of the calculated value as shown in Figure 5. The arrangement of II-type staggered band of the Cu$_3$N/MoS$_2$ heterojunction was conducive to the charge separation of electrons in the heterojunction because the Fermi level of Cu$_3$N was higher than that of MoS$_2$. After the two materials adhered to form the heterojunction, the interface electrons flowing into Cu$_3$N from MoS$_2$ increased the number of electrons in the Cu$_3$N layer and caused additional holes in the MoS$_2$ layer. These conditions
changed the optical band gap. The formed heterojunction can be applied to various high-performance photoelectric devices, such as photocatalysts and photodetectors.

The UV-vis transmission spectrum and diagram of band gap calculation of the Cu$_3$N/MoS$_2$ heterojunction are shown in Figure 6. The transmittance of the pure Cu$_3$N layer in the wavelength range of 350–650 nm was clearly improved after a heterojunction was formed between Cu$_3$N and MoS$_2$. According to the transmission spectrum curve of the thin film, the $E_g$ of Mo-Cu based compound region can be calculated using the optical constant law (3) and Tauc Equation (4) as follows [31]:

$$\alpha = \ln(100/T)/d$$  \hspace{1cm} (3)

$$(a\nu)^2 = A(\nu - E_g)$$  \hspace{1cm} (4)

where $T$ represents the transmittance, $d$ denotes the film thickness, $\alpha$ indicates the absorption coefficient, $\nu$ refers to the photon energy, and $A$ signifies the constant. The band gap $E_g$ could be inferred from the relationship curve between $(a\nu)^2$ and $\nu$ by linearly fitting the straight part of the curve as shown in Figure 6b. The optical band gaps of the Cu$_3$N layer, MoS$_2$ layer, and Cu$_3$N/MoS$_2$ Mo-Cu-based compound region were 1.83, 2.43, and 1.98 eV, respectively.

![Figure 6. (a) Ultraviolet-visible (UV-vis) transmission spectrum of the Cu$_3$N/MoS$_2$ heterojunction and (b) determination of optical band gap of the Cu$_3$N/MoS$_2$ heterojunction.](image)

4. Conclusions

Cu$_3$N/MoS$_2$ heterojunction was prepared on silicon and quartz substrates through magnetron sputtering. Microstructure analysis revealed the good crystallinity of MoS$_2$ and Cu$_3$N in the heterojunction, the uniform distribution of spherical grains on the surface, the thickness of the heterojunction at approximately 50 nm, and the formation of a heterojunction structure with a clear interface. This work provided a simple and effective method for preparing heterojunctions. XPS and UV correlation spectra and data revealed that the prepared Cu$_3$N/MoS$_2$ heterojunction had an arrangement of II-type staggered band. The VBO and CBO of the Cu$_3$N/MoS$_2$ interface were 1.42 and 0.82 eV, respectively. This condition facilitated the charge separation of electrons in MoS$_2$. The prepared heterojunction can be applied to various high-performance photoelectric devices, such as photocatalysts and photodetectors.

Author Contributions: Formal analysis, C.G.; investigation, X.C.; writing—original draft preparation, L.Z.; writing—review and editing, Y.C. and A.J.; supervision and funding acquisition, J.X. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the National Natural Science Foundation of China, grant number 11364011, and the Guangxi Natural Science Foundation, grant number 2017GXNSFAA 198121.

Conflicts of Interest: The authors declare no conflicts of interest.
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