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Large-area MoS$_2$-MoO$_x$ heterojunction thin-film photodetectors with wide spectral range and enhanced photoresponse

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ABSTRACT

We report the enhanced photoresponse in MoS$_2$-MoO$_x$ heterojunction thin film structures on SiO$_2$/Si substrates to demonstrate the feasibility of using them as highly responsive photodetectors with a wide spectral range from visible to near-ultraviolet light. Vertically stacked MoS$_2$-MoO$_x$ heterojunction structures were obtained through two-step chemical vapor deposition composed of MoO$_x$ thin film deposition and subsequent sulfurization of the topmost region of as-deposited MoO$_x$ into MoS$_2$. The formation of heterojunction structures was revealed by transmission electron microscopy and x-ray photoelectron spectroscopy analysis. Under an incident light of 405 nm and 638 nm in wavelength, our MoS$_2$-MoO$_x$ heterojunction thin film structures exhibited significantly higher absorbance, photoresponsivity, and specific detectivity than MoO$_x$ thin films. Moreover, a highly uniform photoresponse was obtained throughout heterojunction thin film structures. These results demonstrate that MoS$_2$-MoO$_x$ heterojunction thin film structures can be a potentially promising material system scalable into large-area photodiode arrays to build active-matrix high-energy-selective photodetectors.

There is a great interest in ultraviolet (UV) photodetectors used in various sensing, imaging, and other optoelectronic applications. UV photodetectors based on one- or two-dimensional nanoscale semiconductors are especially promising because of their intriguing optoelectronic properties. So far, various nanoscale semiconductors with wide bandgaps have been used in UV photodetectors including Ga$_2$O$_3$, In$_2$O$_3$, SnO$_2$, ZnO, and MoO$_x$ ($x < 3$). To further improve the device performance of these photodetectors, the use of heterojunction structures such as MoO$_x$-Si has been suggested. However, the quest to find proper heterojunction materials for UV photodetectors is still ongoing.

Meanwhile, recent progress in research on photodetectors based on two-dimensional transition metal dichalcogenides such as MoS$_2$ nanostructures provides a very compelling case for MoS$_2$-MoO$_x$ heterojunction structures. MoS$_2$ has an energy bandgap in the range of 1.2–1.8 eV depending on its thickness and has a layered crystal structure. Transition metal oxide MoO$_x$ has a wide bandgap of ~3 eV and has a layered crystal structure similar to that of MoS$_2$. Because of the structural compatibility between MoS$_2$ and MoO$_x$ combined with different energy bandgaps, MoS$_2$-MoO$_x$ heterojunction structures allowed for interesting electrical properties for electrical contacts, memristive switches, and photocatalytic hydrogen production. However, little attention has been given to the feasibility of using MoS$_2$-MoO$_x$ heterojunction structures as photodetectors.

Here, we present for the first time MoS$_2$-MoO$_x$ heterojunction structures as highly responsive photodetectors with a wide spectral response from visible to near-UV light. Moreover, whereas previous MoS$_2$-MoO$_x$ heterojunction structures in the literature are based on small MoS$_2$ flakes, we build our MoS$_2$-MoO$_x$ heterojunction structures with large-area chemical vapor deposition (CVD) thin films. We characterize the structure and properties of MoS$_2$-MoO$_x$ heterojunction structures by atomic force microscopy (AFM), scanning electron microscopy (SEM),
transmission electron microscopy (TEM), x-ray photoelectron spectroscopy (XPS), Raman spectroscopy, and UV-visible/near-infrared (UV-Vis/NIR) spectroscopy. We also compare the photoresponsivity and specific detectivity of our MoS$_2$-MoO$_x$ thin film heterojunction structures with those of MoO$_x$ thin films to demonstrate the enhanced performance of MoS$_2$-MoO$_x$ heterojunction structures. We further show a uniformly high photoresponse in our large-area heterojunction thin film structures, providing potentially important implications on their scalability into various large-area optoelectronic devices.

Figure 1(a) illustrates the schematic configuration of the CVD system used to synthesize MoS$_2$-MoO$_x$ hybrid thin film structures. MoO$_x$ and S powders (5 mg each; Sigma-Aldrich Co., 99.98%) were used to synthesize MoS$_2$-MoO$_x$ heterojunction thin film structures. In a two-zone furnace, a (0001)-oriented sapphire or SiO$_2$/Si substrate was placed downstream at zone 2 facing normal to Ar gas flow (100 SCCM). A crucible containing MoO$_x$ powder was placed upstream at zone 1. Another crucible with S powder was placed at 10 mm outside from the upstream entry of zone 1, which allows sulfur to start vaporize after MoO$_x$ predeposition on substrates. For the deposition of MoO$_x$ thin films, only MoO$_x$ powder was used. Zone 1 of the furnace was heated to 750 °C within 15 min at a heating rate of 48.33 °C/min and maintained at 750 °C for 1 h. Zone 2 of the furnace was heated to 650 °C within 15 min at a heating rate of 41.67 °C/min and maintained at 650 °C for 1 h. The working pressure was set to 550 mTorr for the duration of the growth process. Both zones of the furnace were cooled with Ar gas flow (100 SCCM), and when the temperature of the furnace was cooled down to 590 °C, the furnace was opened.

Unlike a previous report, the rapid heating rate of evaporation zone allows the evaporation of MoO$_x$ powder and the predeposition of MoO$_x$ on a vertically standing substrate before sulfur evaporates. After the temperature of the area where sulfur is located becomes sufficiently higher than sulfur melting temperature, sulfur powder starts to vaporize and the top surface of as-deposited MoO$_x$ is sulfurized into MoS$_2$. Because of the limited sulfur diffusion into MoO$_x$, the thickness of MoS$_2$ and MoO$_x$ can be controlled if conditions including temperature and location of precursors are maintained at aforementioned conditions. Figure 1(b) shows actual MoS$_2$-MoO$_x$ thin films on a Si/SiO$_2$ substrate (~2 × 3 cm$^2$). Continuous thin films of MoS$_2$-MoO$_x$ are formed on the substrate, size of which is only limited by the diameter of the quartz tube (5 cm) in the CVD system. Thin films are not deposited on the lower region of the substrate, which is vertically inserted into a holder during deposition. As shown in Fig. 1(c), AFM analysis indicates a fairly smooth surface of MoS$_2$-MoO$_x$ heterojunction thin films with a root-mean-square roughness of 2.17 nm. A cross-sectional TEM image in Fig. 1(d) clearly reveals the formation of heterojunction thin film structures composed of two distinguishable films stacked vertically (upper film of 5.86 nm and lower film of 15.58 nm thickness). A typical layered structure of MoS$_2$ can be found in the upper film, confirming the intended sulfurization of the upper layer of predeposited MoO$_x$. A point energy-dispersive x-ray spectroscopy (EDS) analysis of TEM indicates an Mo to S atomic ratio of 1:1.77 in the upper film, further confirming the formation of MoS$_2$. Figure 2(a) shows the Raman spectra of MoS$_2$-MoO$_x$ heterojunction thin film structures. Two characteristic Raman modes of MoS$_2$ (E$_{2g}$(in-plane vibration of Mo atom to S atom) and A$_{1g}$(out-of-plane vibration of S atoms) modes, can be found at 382.27 and 408.14 cm$^{-1}$, respectively. The frequency difference between the two characteristic Raman modes is 25.86 cm$^{-1}$, confirming the multilayer nature of MoS$_2$. Raman modes associated with MoO$_x$ can
also be found at \(-458\) cm\(^{-1}\), suggesting the existence of underlying MoO\(_x\) layers.

XPS spectra of MoS\(_2\)-MoO\(_x\) heterojunction thin film structures also suggest the presence of MoO\(_x\) layers underneath MoS\(_2\). Figures 2(b) and 2(c) show the evolution of the Mo 3d spectra of MoS\(_2\)-MoO\(_x\) heterojunction thin film structures with depth profiling. In Fig. 2(b), obtained from the top surface, strong doublet peaks at 229.42 and 232.55 eV correspond to Mo\(^{4+}\) 3d states of MoS\(_2\).\(^{24-26}\) S 2s peak of MoS\(_2\) also appears at 226.57 eV.\(^{27}\) The additional doublet peaks with low intensity at relatively higher binding energies of 232.69 and 235.82 eV correspond to Mo\(^{6+}\) 3d states of underlying MoO\(_x\).\(^{28}\)

In Fig. 2(c), obtained from the inner MoS\(_2\) region, strong Mo\(^{4+}\) 3d doublet peaks are still observed, but the intensity of Mo\(^{6+}\) 3d doublets increases, suggesting the increased detection of underlying MoO\(_x\). In Fig. 2(d), S 2p doublets of the top surface at 162.23 and 163.41 eV correspond to MoS\(_2\). Overall, XPS analysis suggests the formation of MoS\(_2\)-MoO\(_x\) heterojunction thin film structures, which is consistent with TEM analysis.

The optical absorbance of MoO\(_x\) thin films and MoS\(_2\)-MoO\(_x\) heterojunction thin film structures on sapphire substrates is measured by UV-visible-NIR spectroscopy from 200 nm to 800 nm in wavelength at room temperature. In Fig. 3(a), the absorbance of MoO\(_x\) thin films is prominent at a wavelength shorter than \(-350\) nm. The optical energy bandgap of MoO\(_x\) thin films is estimated to be \(-3.91\) eV based on the following equation:\(^{29}\) \((\alpha h\nu)^2 = B(h\nu - E_g)^2\), where \(\alpha\), \(h\nu\), \(B\), and \(E_g\) are absorbance, photon energy, constant, and energy bandgap, respectively.

Thin film structures, overall absorbance resembles that of MoS\(_2\), suggesting that absorbance is dominated by MoS\(_2\) except at very short wavelengths (\(<350\) nm). Absorbance due to excitonic transitions of MoS\(_2\) [(a) and (b)]\(^{12,14}\) can be observed along with absorbance associated with the van Hove singularity of MoS\(_2\) [(c) and (d)].\(^{7}\) As the existence of the van Hove singularity can enhance visible and UV light absorption, it can allow MoS\(_2\)-MoO\(_x\) heterojunction thin film structures to respond to broader spectral range than MoO\(_x\) thin films.

To measure photoresponse, MoS\(_2\)-MoO\(_x\) heterojunction thin film structures and MoO\(_x\) thin films with patterned electrodes are illuminated by light at right angles as shown in Fig. 3(b). Figures 3(c) and 3(d) show photocurrent \(I_{\text{photo}} = I_{\text{light}} - I_{\text{dark}}\) (current with light) – (current in the dark) of each thin film under an incident laser of 405 nm (3.06 eV) and 638 nm (1.94 eV) in wavelength, respectively, at a laser power of 1 mW cm\(^{-2}\). MoO\(_x\) thin films show very low photocurrent at both wavelengths. This is not surprising as incident photon energy is insufficient to excite electrons in the valence band across the bandgap of MoO\(_x\) thin films (\(-3.91\) eV). By contrast, the photocurrent of MoS\(_2\)-MoO\(_x\) heterojunction thin film structures is higher than that of MoO\(_x\) thin films at both wavelengths because laser photon energy is higher than the energy bandgap of multi-layer MoS\(_2\) (\(-1.2\) eV).\(^{12,14}\) As the photon energy of the incident laser is smaller than the energy bandgap of MoO\(_x\), absorption of heterojunction structures will be dominated by MoS\(_2\). In particular, the photocurrent of MoS\(_2\)-MoO\(_x\) heterojunction thin film structures is higher at 405 nm than at 638 nm. This can be understood by the higher absorbance of MoS\(_2\) at 405 nm than that at 638 nm.
Our MoS$_2$-MoO$_x$ heterostructures also showed high photocurrent under a UV lamp (365 nm, 3.40 eV) at a power density of 20 $\mu$W cm$^{-2}$ (Figure S1 in the supplementary material). These photocurrent measurements suggest that MoS$_2$-MoO$_x$ heterojunction thin film structures can respond to a wider range of optical wavelengths than MoO$_x$ thin films, which is consistent with absorbance measurements.

A primary figure of merit for photodetectors is photoresponsivity ($R_{ph}$), which is a measure of electrical response to light. $R_{ph}$ is given by $R_{ph} = I_{\text{photo}}/(P_{\text{inc}} \times S)$, where $I_{\text{photo}}$, $P_{\text{inc}}$, and $S$ are the photocurrent, areal power density of the incident light, and irradiated area, respectively. In Fig. 3(e), $R_{ph}$ of MoS$_2$-MoO$_x$ heterojunction thin film structures and MoO$_x$ thin films is plotted as a function of $P_{\text{inc}}$ under 405-nm and 638-nm laser (drain voltage $V_{ds} = 10$ V). Under 405-nm laser, MoS$_2$-MoO$_x$ heterojunction structures show nearly 60 times higher $R_{ph}$ (up to $\sim 1.09$ A W$^{-1}$) than MoO$_x$ thin films. Under 638-nm laser, MoS$_2$-MoO$_x$ heterojunction structures show 30 times higher $R_{ph}$ ($\sim 10$ mA W$^{-1}$) than MoO$_x$ thin films. The higher $R_{ph}$ under 405-nm light than that under 638-nm light may be explained by the higher absorbance at 405 nm than that at 638 nm.
at 638 nm in Fig. 3(a). The higher absorbance will generate more electrons and holes, resulting in higher photocurrent (photoconductive effect). Although $R_{th}$ in this work is lower than those of MoS$_2$ photodetectors based on single crystal flakes, $^{3,32}$ it is still comparable with those of MoS$_2$ photodetectors based on thin films (1 mA W$^{-1}$–1 A W$^{-1}$) $^{33–36}$ and MoO$_3$ photodetectors (1 mA W$^{-1}$–10 A W$^{-1}$) $^{33,37,38}$ in the literature.

Another primary figure of merit of photodetectors is specific detectivity ($D^*$), which is a measure of detector sensitivity. With the assumption that shot noise from dark current dominates total noise, $D^*$ is calculated by $D^* = R_{ph}S/(2eI_{dark})^{1/2}$, where $e$ is the unit charge. Figure 3(f) shows the calculated $D^*$ of MoS$_2$–MoO$_x$ heterojunction thin film structures and MoO$_3$ thin films as a function of $P_{inc}$ under 405-nm and 638-nm laser (drain voltage $V_{ds} = 10$ V). At 405 nm, MoS$_2$–MoO$_x$ heterojunction structures show nearly 550 times higher $D^*$ ($\sim 2.08 \times 10^{11}$ Jones) than MoO$_3$ thin films. Under 638-nm light, MoS$_2$–MoO$_x$ heterojunction structures exhibit maximum $D^*$ of $\sim 6 \times 10^5$ Jones, which is more than 100 times higher than MoO$_3$ thin films. The higher $D^*$ at 405 nm is partly due to the increased photocurrent at 405 nm as discussed in the above paragraph. The calculated $D^*$ values are comparable with those of MoS$_2$ photodetectors based on thin films ($10^9–10^{10}$ Jones) $^{33–36}$.

We also measure the photoswitching response times (rise time and fall time) of MoS$_2$–MoO$_x$ heterojunction thin film structures under 405-nm and 638-nm laser, respectively (drain voltage $V_{ds} = 3$ V). We define the rise time as the time required to switch photocurrent from 10% to 90% of maximum and the fall time as that from 90% to 10% of maximum. In Fig. 3(g), under 405-nm light, rise time of 9.8 s and fall time of 12.6 s are obtained in our MoS$_2$–MoO$_x$ heterojunction thin film structures. Interestingly, under 638-nm light, MoS$_2$–MoO$_x$ heterojunction thin film structures show faster rise time and fall time (52 ms each) than those under 405-nm light. Although these response times are not very impressive, they are still comparable with those of MoS$_2$ photodetectors (10 µs–10 s) $^{3,35}$ and MoO$_3$ photodetectors (100 ms–100 s) $^{33,37,38}$ in the literature.

The higher $R_{ph}$ and slower response times at 405 nm than those at 638 nm may suggest photogating effect in MoS$_2$–MoO$_x$ heterojunction structures. When MoS$_2$–MoO$_x$ heterostructures are formed, the difference in the work function will cause band bending at the junction (Fig. S2a–b in the supplementary material). Under low-energy incident light, the entrapment of photogenerated holes in the localized interface sites will effectively apply gate voltage (photogating effect), which will reduce the energy barrier between source and drain electrodes and increase photocurrent (Fig. S2c). Under high-energy incident light, electron-hole pairs are also generated in MoO$_3$. As more photogenerated holes will be trapped, more electrons will transfer from MoO$_3$ to MoS$_2$, further increasing the photocurrent (Fig. S2d). However, the higher photoresponse by photogating effect is obtained at the expense of slower response time. Under 405-nm light, the high density of trapped holes at MoS$_2$–MoO$_x$ heterojunction will allow slower response times (but higher $R_{ph}$). By contrast, under 638-nm light, the low density of trapped holes at the MoS$_2$–MoO$_x$ heterojunction will allow relatively faster response times (but lower $R_{ph}$). However, more systematic investigation is needed to understand this in the future.

We further measure the photocurrent of MoS$_2$–MoO$_x$ heterojunction thin film structures in a 3 × 5 device array configuration to evaluate its uniformity (drain voltage $V_{ds} = 10$ V). Figure 4(a) shows the actual patterned device array. In Figs. 4(b) and 4(c), each device shows a similar range of $I_{photo}$ regardless of its position in a 3 × 5 array. Under 405-nm light, 10 of 15 devices show $I_{photo}$ above 13 nA and the average $I_{photo}$ of all the devices ($\sim 16.5$ nA) is in good agreement with a single device shown in Fig. 3(c). Under 638-nm light, all the devices show $I_{photo}$ in the range of 1–5 nA and the average $I_{photo}$ of all the devices ($\sim 1.93$ nA) is consistent with $I_{photo}$ of a single device shown in Fig. 3(d). These results suggest the feasibility of using MoS$_2$–MoO$_x$ heterojunction thin film structures, with proper scalability technology, as highly uniform, reliable, and large-area device arrays for active-matrix or broad wavelength-selective sensor applications.
In summary, we synthesized large-area MoS$_2$-MoO$_x$ heterojunction thin film structures on SiO$_2$/Si substrates for high response photodetectors. An MoS$_2$ layer of ~5 nm thickness was formed on top of the MoO$_x$ layer by a two-step CVD process composed of MoO$_x$ thin film deposition and subsequent sulfurization of MoO$_x$ into MoS$_2$. The structure and properties of MoS$_2$-MoO$_x$ heterojunction were characterized by AFM, SEM, TEM, XPS, Raman spectroscopy, and UV-visible/NIR spectroscopy. Compared to MoO$_x$ thin films, our MoS$_2$-MoO$_x$ heterojunction thin film structures exhibited significantly higher photoresponsivity (R$_{ph}$) and specific detectivity (D') under light illumination over a wide range of wavelengths between 405 nm and 638 nm. MoS$_2$-MoO$_x$ heterojunction thin film structures also showed comparable response times with MoS$_2$ and MoO$_x$ photodetectors in the literature. The highly uniform photoreponse of our MoS$_2$-MoO$_x$ heterojunction thin film structures suggests their potential scalability into large-area arrays of photodetectors.

See supplementary material for photocurrent under UV and energy band diagrams.

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REFERENCES