Solar-Blind UV Photodetector Based on Atomic Layer-Deposited Cu₂O and Nanomembrane β-Ga₂O₃ pn Oxide Heterojunction

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ABSTRACT: Herein, we present a solar-blind ultraviolet photodetector realized using atomic layer-deposited p-type cuprous oxide (Cu₂O) underneath a mechanically exfoliated n-type β-gallium oxide (β-Ga₂O₃) nanomembrane. The atomic layer deposition process of the Cu₂O film applies bis(N,N′-di-secbutylacetamidinate)dicopper(1) [Cu(5Bu-Me-amd)₂] as a novel Cu precursor and water vapor as an oxidant. The exfoliated β-Ga₂O₃ nanomembrane was transferred to the top of the Cu₂O layer surface to realize a unique oxide pn heterojunction, which is not easy to realize by conventional epitaxy techniques. The current−voltage (I−V) characteristics of the fabricated pn heterojunction diode show the typical rectifying behavior. The fabricated Cu₂O/β-Ga₂O₃ photodetector achieves sensitive detection of current at the picoampere scale in the reverse mode. This work provides a new approach to integrate all oxide heterojunctions using membrane transfer and bonding techniques, which goes beyond the limitation of conventional heteroepitaxy.

INTRODUCTION

Solar-blind ultraviolet (UV) photodetectors have been actively investigated recently because of their variety of potential applications in the fields of military surveillance, biological/chemical analyses, astronomical observations, and optical communications. Recently, photonic devices based on various materials have been widely investigated due to their intrinsic properties, including high transparency and excellent sensitivity. Among the oxide-based materials, especially, cuprous oxide (Cu₂O) is a natural p-type semiconductor with a bandgap of 2.1 eV that can be photoexcited in the UV/visible spectral region. Moreover, it exhibits unique properties such as high absorption efficiency, non-toxicity, abundant availability, and low production costs. The atomic layer deposition (ALD) process is particularly suited for oxide materials growth with a variety of applications in high-k gate dielectric and highly scaled dynamic random access memory capacitor integration because of its conformal step coverage and atomic layer thin thickness control. Although many studies of the ALD growth of metallic Cu have been reported, only a few studies related to ALD grown Cu₂O have been performed. As determined from their bandgaps, binary compound semiconductors including GaN, SiC, and ZnO are suitable for developing visible-blind UV detectors, which are required for higher responsivity in the UV range compared to lower energy ranges. To meet the criteria of a solar-blind photodetector with a cutoff wavelength below 280 nm, alloy engineering is used to tune the bandgap as high as 4.42 eV to eliminate the longer wavelength. For instance, AlGaN and MgZnO wide bandgap (WBG) ternary semiconductor alloys were used to develop solar-blind photodetectors, achieving rapid progress for the development of high-performance avalanche solar-blind photodetectors with improved photoresponsivity and response speed. However, these materials required a high growth temperature above 1350 °C. The phase segregation from wurtzite to rock salt structure results in the degradation of detecting performance. Alternatively, ultra-WBG (UWBG) β-Ga₂O₃ semiconductors have been actively developed for UV-transmitting optoelectronic applications owing to their UWBG of 4.8–4.9 eV, the availability of large-size β-Ga₂O₃ bulk single crystals, and homoeptaxial growth of high crystalline quality epitaxial layers with the possibility for doping and bandgap engineering. In particular, the exfoliated β-Ga₂O₃ nanomembrane transfer technique offers the opportunity to demonstrate some of the prototype device concepts, which are usually difficult to realize using conventional material growth techniques.

Herein, we demonstrate a heterojunction photodetector by integrating ALD-grown p-type Cu₂O with an exfoliated β-Ga₂O₃ nanomembrane to form a suspended pn heterojunction structure. The ALD process can be applied for photovoltaic applications, in particular for depositing ultrathin layers at...
The ALD cycle consists of Cu deposition and oxidation, as shown for producing ultrathin fabrication step, a Cu2O thin
fabrication process is listed in Figure 1a. During the deposition features complementarity and self-limitation related to the surface reactions. The former feature involves two reactants for preparation of the surface for its reaction with the other vapor, allowing the deposition cycles to be repeated. In addition, the latter feature contributes to the very conformable uniform thickness even on nonuniform surface structures.28 For a stable supply, the temperature of the canisters for the Cu precursor and H2O was maintained constant at 130 and 30 °C, respectively. In a single thermal ALD Cu2O cycle, the optimized process consists of a Cu-precursor pulse for 30 ms with a 100 sccm N2 flow, a purge pulse of 11 s with 100 sccm of N2 flow, a water pulse for 60 ms with 100 sccm N2 flow, and a purge pulse of 11 s with 100 sccm of N2 flow. During the ALD processes, the substrate temperature was maintained at the optimized growth temperature of 180 °C (Figure S2 in the Supporting Information) and the observed growth rate was ~0.002 nm/cycle (Figure S3 in the Supporting Information). To improve the ALD growth rate and the film conductivity, plasma-enhanced ALD process with O3 will be introduced in the near future. In the next step, the thin β-Ga2O3 nanomembrane was mechanically exfoliated from the bulk β-Ga2O3 substrate cleavage and transferred to the top of the Cu2O layer on the SiO2/Si substrate, as shown in Figure 1c. β-Ga2O3 nanomembrane is n-type with a Sn-doping concentration of 2.7 × 1018 cm−3. The AZ1518 positive photoresist (PR) with a thickness of 1.8 μm was coated on the wafer, as shown in Figure 1d. To form two metal contacts on both the p-type Cu2O film and n-type β-Ga2O3 flake, Cu2O and SiO2 layers were etched using a 6:1 HF solution for 60 min, as shown in Figure 1e. The PR acts as a hardmask to protect the Cu2O film underneath the PR, while Cu2O and SiO2 were etched simultaneously. As shown in Figure 1g, two 100 nm Ni electrodes were deposited on the p-type Cu2O film and n-type β-Ga2O3 nanomembrane. Figure 1g shows an optical image of the fabricated device with a 250 nm thick β-Ga2O3 flake including a 12 nm Cu2O film and Ni electrodes. The contact properties with various metals on the Cu2O film were studied and are summarized in Figure S4 of the Supporting Information. Figure 1h,i shows the current–voltage (I–V) characteristics of the fabricated device. The measured I–V curve of the Cu2O/β-Ga2O3 pn heterojunction presents typical rectifying characteristics as a well-defined diode. The on-current was limited by both contact resistance and interface quality between the two heterogeneous oxide materials. Although the rectifying characteristics resemble the basic function of a pn heterojunction diode, further process optimization is needed to reduce the surface roughness, interface quality, the conductivity of the Cu2O film, and its

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**RESULTS AND DISCUSSION**

Figure 1 shows the schematic illustration of the procedure used for fabricating the Cu2O/β-Ga2O3 pn heterojunction photodetector with a suspended structure. A representative fabrication process is listed in Figure 1a. During the first fabrication step, a Cu2O thin film was deposited on the oxide (270 nm SiO2) of a p+ Si wafer via ALD, as shown in Figure 1b. ALD is one of the most effective oxide growth techniques for producing ultrathin films at atomic layer accuracy. A single ALD cycle consists of Cu deposition and oxidation, as shown in Table S1 of the Supporting Information. In this study, bis(N,N′-di-sec-butylacetamidinato)dicopper(I) [Cu(5Bu-Me-amd)]2 was used as a novel Cu precursor. The structural formula of the Cu precursor is presented in Figure S1 of the Supporting Information. The ALD process for copper deposition features complementarity and self-limitation related to the surface reactions. The former feature involves two reactants for preparation of the surface for its reaction with the other vapor, allowing the deposition cycles to be repeated. In addition, the latter feature contributes to the very conformable uniform thickness even on nonuniform surface structures.28 For a stable supply, the temperature of the canisters for the Cu precursor and H2O was maintained constant at 130 and 30 °C, respectively. In a single thermal ALD Cu2O cycle, the optimized process consists of a Cu-precursor pulse for 30 ms with a 100 sccm N2 flow, a purge pulse of 11 s with 100 sccm of N2 flow, a water pulse for 60 ms with 100 sccm N2 flow, and a purge pulse of 11 s with 100 sccm of N2 flow. During the ALD processes, the substrate temperature was maintained at the optimized growth temperature of 180 °C (Figure S2 in the Supporting Information) and the observed growth rate was ~0.002 nm/cycle (Figure S3 in the Supporting Information). To improve the ALD growth rate and the film conductivity, plasma-enhanced ALD process with O3 will be introduced in the near future. In the next step, the thin β-Ga2O3 nanomembrane was mechanically exfoliated from the bulk β-Ga2O3 substrate cleavage and transferred to the top of the Cu2O layer on the SiO2/Si substrate, as shown in Figure 1c. β-Ga2O3 nanomembrane is n-type with a Sn-doping concentration of 2.7 × 1018 cm−3. The AZ1518 positive photoresist (PR) with a thickness of 1.8 μm was coated on the wafer, as shown in Figure 1d. To form two metal contacts on both the p-type Cu2O film and n-type β-Ga2O3 flake, Cu2O and SiO2 layers were etched using a 6:1 HF solution for 60 min, as shown in Figure 1e. The PR acts as a hardmask to protect the Cu2O film underneath the PR, while Cu2O and SiO2 were etched simultaneously. As shown in Figure 1g, two 100 nm Ni electrodes were deposited on the p-type Cu2O film and n-type β-Ga2O3 nanomembrane. Figure 1g shows an optical image of the fabricated device with a 250 nm thick β-Ga2O3 flake including a 12 nm Cu2O film and Ni electrodes. The contact properties with various metals on the Cu2O film were studied and are summarized in Figure S4 of the Supporting Information. Figure 1h,i shows the current–voltage (I–V) characteristics of the fabricated device. The measured I–V curve of the Cu2O/β-Ga2O3 pn heterojunction presents typical rectifying characteristics as a well-defined diode. The on-current was limited by both contact resistance and interface quality between the two heterogeneous oxide materials. Although the rectifying characteristics resemble the basic function of a pn heterojunction diode, further process optimization is needed to reduce the surface roughness, interface quality, the conductivity of the Cu2O film, and its

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**Figure 1.** Schematic illustration of the fabrication procedure of the Cu2O/β-Ga2O3 photodetector and typical current voltage (I–V) characteristics. (a) Simplified process flow for the fabricated device. (b–f) Show schematics of the proposed atomic layer deposited p-type Cu2O/suspended n-type β-Ga2O3 heterojunction with low dark and photonic currents for highly sensitive photodetector applications.
contact resistance to achieve a higher and better photosensitivity.

The composition and chemical state of the ALD-grown Cu$_2$O film surfaces were investigated via X-ray photoelectron spectroscopy (XPS) with a Kratos Axis Ultra DLD instrument. This is a surface-sensitive technique that can be used to analyze the surface chemical compositions of deposited films, as shown in Figure 2a,b. Figure 2a shows the survey scan XPS spectrum of the as-grown Cu$_2$O film with multiple peaks arising from Cu and O. The high-resolution XPS spectra in the vicinity of the Cu 2p peaks showed two distinct peaks at the binding energies of 932.2 and 951.1 eV, corresponding to the 2p$_{3/2}$ and 2p$_{1/2}$
states of Cu⁺ (Figure 2b). Two broad satellite peaks at 943–948 eV were also observed, both of which were attributed to the Cu²⁺ state (CuO) on the surface. Clear evidence of the ALD-grown Cu₂O film is shown in Figure 2c through the scanning transmission electron microscopy (STEM) analysis and energy-dispersive X-ray spectroscopy (EDS) mapping images. The high-resolution atomic force microscopy (AFM) images of the surface morphologies of the Cu₂O film are shown in Figure 2d. The surface of the film was reasonably smooth with a roughness of approximately 4–5 nm. Figure 2e shows the ALD-grown Cu₂O thin film on the glass substrate. As shown in Figure 2f, the Cu₂O thin film with a thickness of 12 nm exhibited a high transparency of approximately 90%, resulting in light absorption below ~500 nm, corresponding to an energy of approximately 2.4 eV. The thickness of the β-Ga₂O₃ flake was measured by AFM, as illustrated in Figure 2g. The channel width was determined by the width of the flake because of the stochastic nature of the β-Ga₂O₃ exfoliation process. Figure 2h shows the transmittance characteristics of the β-Ga₂O₃ bulk sample used in the fabricated device. The inset of Figure 2h shows the optical image of the β-Ga₂O₃ bulk substrate. The optical transmission characteristics of both the Cu₂O and β-Ga₂O₃ films across the visible range of the spectrum is very high over 80%.

Figure 3a shows a schematic view of the fabricated prototype p-type Cu₂O/n-type β-Ga₂O₃ pn heterojunction photodiode and the time-dependent photoresponse measurement configuration. To clearly illustrate the photoinduced electrical conduction mechanism, the energy band diagrams of the Cu₂O/β-Ga₂O₃ pn heterojunction are provided in Figure 3b–c. The band-gap energies of Cu₂O and β-Ga₂O₃ are 2.1 and 4.8 eV, respectively. The valence band offset (ΔEᵥ = 2.4 eV) and the conduction band offset (ΔEᶜ = 0.3 eV) of the Cu₂O/β-Ga₂O₃ pn heterojunction were calculated. After being physically and electrically contacted, carriers can flow until both the Fermi levels align, and a pn heterojunction depletion layer formed near the interface of Cu₂O/β-Ga₂O₃. As shown in Figure 3c, when UV light irradiates the fabricated device, the light passes into the interface of the Cu₂O/β-Ga₂O₃ pn heterojunction and generates electron–hole pairs (ehp). In the fabricated device, the β-Ga₂O₃ film was doped with Sn at a concentration of 2.7 × 10¹⁸ cm⁻³, so the separation of the photogenerated carriers by incident light is more effective and faster due to the larger conduction band offset. When a positive (+) bias was applied to the Cu₂O side, electrons were transported toward the p-type Cu₂O. Both UV light with an intensity of 2.5 mW (λ = 390 nm) and visible light with an intensity of 10 W (λ = 400–700 nm) were used under the illumination of a fixed light intensity. The I_ON/I_OFF ratios with various applied voltages are described in Figure S5 of the Supporting Information. Figure 3d,e shows the photocurrent characteristics in the forward mode of the Cu₂O/β-Ga₂O₃ device under UV and visible light, respectively. Four repeat on–off cycles of the light source were used to examine the repeatability of the fabricated device under various applied voltages (V_app) from 5 to 20 V. Figure 3d,e shows the continuous time-dependent photoresponse characteristics in the forward mode of the Cu₂O/β-Ga₂O₃ device under various V_app conditions irradiated with UV and visible light, respectively. A switching period of 30 s was used for turning the light on and off sequentially. As shown in Figure 3f, the measured photocurrent drastically increases under UV light irradiation because the photogenerated carriers are significantly limited by visible light ranging from 400 to 700 nm.

Figure 4a shows the representative current–voltage characteristics under the reverse mode of the Cu₂O/β-Ga₂O₃ photodetector under various V_app conditions in the dark at room temperature (20 °C). The zero dark current is observed at an applied bias of approximately 8 V. As in previous measurements, the photodetector is exposed to light, the induced photocurrent increases rapidly. In contrast, when the light is switched off, the light-induced photocurrent rapidly decreases. However, no photocurrent was generated by the visible light with a longer wavelength than that of UV light in
the two cases, as shown in Figure 4b,c. The induced photocurrent is directly attributed to the absorption of UV photons. The response and recovery time of the fabricated device under reverse biases are both estimated to be approximately 200 ms, as shown in Figure S6 of the Supporting Information. These fast response characteristics indicate that the fabricated Cu2O/β-Ga2O3 pn heterostructure is promising for the detection of fast optical signals, with superior performance compared to that of previously developed oxide-based photodetector devices. To quantitatively assess the device performance of the fabricated device, the responsivity (R) and detectivity (D) were calculated as shown in Figure 4d. The R and D at an applied voltage of −16 V were estimated to be 53 mA·W−1 and 5.2 × 1012 cm·Hz1/2/W, respectively. In the two equations in the inset of Figure 4d, Iph and ID are the measured current under photonic and dark states, Pph is the light intensity, A is the effective illuminated area (=8 × 10−3 cm2), and e is the electric charge (=1.6 × 10−19 C). Meanwhile, although we investigated the characterization of a solar-blind UV photodetector using a single wavelength of 390 nm, comprehensive studies using the light source with a wide range of wavelengths is required for more practical applications as a further study.

# CONCLUSIONS

We have successfully developed the thermal ALD process of p-type Cu2O and integrated it with mechanically exfoliated n-type β-Ga2O3 as a hybrid pn heterojunction solar-blind UV photodetector. The p-type Cu2O film is an important building block for all oxide-based electronic and photonic device research. In particular, the low temperature of the ALD process offers the unique opportunity to develop back-of-the-line transistor technology, even for mainstream Si-based CMOS applications. Inspired by the widely adopted two-dimensional van der Waals heterogeneous integration, this work provides a feasible route to integrate oxide-based pn heterojunctions for various device applications, which were previously limited by the challenging heterogeneous epitaxy techniques.

# EXPERIMENTAL METHODS

Device Fabrication. The p-type Cu2O thin film was deposited on 90 nm SiO2/Si substrates by the ALD process with optimized conditions. The n-type β-Ga2O3 flakes were transferred onto the Cu2O thin film by the exfoliation technique. Subsequently, Ni metal electrodes were formed by electron beam evaporation and lift-off process after photolithography patterning. The 6:1 HF solution was used not only to etch the Cu2O film underneath the β-Ga2O3 flake but also to deposit each metal electrodes onto the p-type Cu2O and n-type β-Ga2O3 flake, respectively.

Experimental Equipment. All electrical measurements were carried out in an ambient air environment without any device encapsulation. The electrical I–V characteristics were measured by using a B1500A semiconductor device analyzer. An AFM (model Veeco Dimension 3100) analysis was also conducted to assess the surface roughness of the atomic layer deposited Cu2O film.

TEM Analysis. To confirm the well-deposited Cu2O film layer, high-resolution TEM (FEI TALOS F200X operated at 200 kV) equipped with high angle annular dark field detectors and super X electron-dispersive X-ray spectroscopy was carried out.

XPS Analysis. The chemical composition of the Cu2O film was investigated using the XPS system (Kratos Axis Ultra DLD) with monochromatic Al Kα radiation (1486.6 eV).

Transmittance Measurement. The transmittance of Cu2O, β-Ga2O3, and the glass substrate was evaluated using Filmetrics F20 with a wavelength range from 380 to 1050 nm.

# ASSOCIATED CONTENT

# Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.9b03149.

## Notes

The authors declare no competing financial interest.

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