

Photodetection Performance Enhancement of Crystal-like Co_3O_4 Nanostructure Synthesized via Pulsed Laser Deposition

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ABSTRACT

Crystal-like Cobalt Oxide (Co_3O_4) nanostructures synthesized on a Copper Oxide (CuO) layer can enhance charge separation and improve the optoelectronic properties. To achieve a high response photodetector, copper oxide (CuO) thin films were used to match the quartz substrate with (Co_3O_4), which leads to the high-density, crystal-like of Co_3O_4 nanostructures using a combination of thermal evaporation and pulsed laser deposition (PLD) techniques. Copper (Cu) was first deposited on quartz substrates via thermal evaporation under vacuum conditions and subsequently oxidized at 700 °C to form CuO. and then in the next stage, cobalt (Co) was deposited using Pulsed Laser Deposition (PLD) technique, which is followed by oxidation process at temperatures up to 900 °C to grow the desired crystal-like Co_3O_4 nanostructures. X-ray diffraction (XRD) and Field Emission Electron Microscopy (FE-SEM) were used to investigate the structural and morphological properties of the produced films; optical properties using UV-visible spectroscopy were also investigated. Crystal-like Co_3O_4 exhibited significantly improved current-voltage (I-V) characteristics, with high detectivity. The dark current and photocurrent of the metal-semiconductor-metal (MSM) photodetector fabricated on Co_3O_4 were 8.14 μA and 442 μA , respectively. Response and recovery times of 7.4 s and 9.1 s for this detector. An MSM photodetector with aluminum (Al) contact electrodes was fabricated on both layers. The rectifying behavior of I-V curve, suggesting that the surface states or defect levels in Co_3O_4 are relatively low.

Keywords: Co_3O_4 , Crystal-like Co_3O_4 nanostructures growth decorated by CuO, Nanocrystal morphology, Visible light detectivity

1. INTRODUCTION

The most important components in a wide range of advanced technologies are the Photodetectors, such as optical communication systems, environmental monitoring platforms, and biomedical imaging applications. [1]. Semiconductor metal oxides (SMOs) have attracted significant attention in researches due to their stability, cost-effectiveness, and tunable optoelectronic properties. Which are they exhibit remarkable characteristics in the nanostructures such as a large surface area, adjustable chemical reactivity, controllable particle size, and excellent redox behavior. [1-4]. Cobalt oxide (Co_3O_4) one of these semiconductor oxides. Has attracted significant interest as a key material for photodetector applications owing to its unique properties, including an optical absorption edge that spans the visible to ultraviolet (UV) region, a relatively narrow bandgap (~1.2–2.0 eV), and a favorable electronic structure. Furthermore, Co_3O_4 can be synthesized using simple, cost-effective methods and demonstrates excellent stability under various environmental conditions. [2]. A number of extensive efforts have been devoted to synthesizing Co_3O_4 nanostructures on different substrates. [1-9]. Sol-Gel technique was employed to synthesize cobalt oxide [4], Co_3O_4 nanoparticles were successfully prepared through thermal decomposition of cobalt glycerolate in a controlled oxygen/nitrogen atmosphere [10]. Powder metallurgy method was utilized to synthesize CuO-CoO nanocomposite [1], preparation of cobalt oxide/copper

oxide composites for gas sensing application using a simple sol-gel process[11], Green synthesis of Cobalt oxide nanoparticles via *Aspalathus linearis* [12], With the increased contemporary interest in nanoscale materials, [2] investigated Co_3O_4 nanoparticles by means of neutron scattering and found how the theory of critical phenomena breaks down in the nanoscale regime, porous Co_3O_4 nanowalls were deposited on graphene foam by a simple hydrothermal process[13]. Recently, there has been a lot of interest in Co_3O_4 nanostructures because of their high optical gain, which preferred for optoelectronics and sensing applications. It appears that the interface between the Co_3O_4 and substrate is the limiting issue for using it as active layer in the devices that have been reported. The lattice mismatch between Co_3O_4 and most of the tested substrates may be the cause of this limitation. In order to prevent lattice mismatch and improve the crystallization of Co_3O_4 nanostructure, the current study suggested using a thin film of Copper oxide (CuO), as buffer layer.

As a p-type semiconductor with a narrow bandgap (~1.2 eV), it exhibits strong absorption in the visible and infrared regions, making it a promising candidate for photodetection applications. [8, 14-16].

As a result of Co_3O_4 , tunable bandgap, efficient charge carrier mobility and separation, the fabrication of Co_3O_4 , on CuO photodetectors shows significant potential for enhancing performance. The influence of the CuO layer's on the growth, crystallinity, and charge transport behavior of

Co₃O₄ remains largely unexplored. The CuO layer may significantly affect the nucleation sites, crystal orientation, and defect states of the Co₃O₄ film, leading to more effective charge separation and enhancing photodetection efficiency.

This study aims to introduce an approach to overcome the challenges in synthesizing Co₃O₄ nanostructures on CuO layer and determine the functional role of this layer on the Co₃O₄ morphology, charge dynamics, and photodetector performance. In addition to create an ideal heterostructure for next-generation high-performance photodetectors by investigating how these materials interact.

2. EXPERIMENTAL PROCEDURE

After cleaning, the quartz substrates were placed on the substrate holder at a distance of 20 cm from the tungsten boat containing high-purity copper powder. The copper was then thermally evaporated onto the substrates under a vacuum of 2.2×10^{-5} mbar using a vacuum thermal evaporator. The resulting Cu/quartz sample was subsequently transferred into a thermal tube furnace for oxidation at 700°C, and the sample was cooled to room temperature to form CuO. The resulting CuO/quartz film was then used as the substrate to grow Co₃O₄ nanostructures.

Cobalt oxide (Co₃O₄) thin films were fabricated using the pulsed laser deposition (PLD) technique. A Nd:YAG laser with a 10 ns pulse width system setup was used to ablate a high-purity cobalt metal target. In a vacuum chamber at a base pressure of 4.6×10^{-5} mbar, and the laser beam was focused using the 50 cm focal length plano-convex lens the deposition was performed.

Cobalt (Co/CuO/quartz) thin film was then transferred into a thermal tube furnace for oxidation at 700°C followed by cooling to room temperature to produce Cobalt oxide (Co₃O₄) thin film.

Aluminum (Al) metal mask using vacuum thermal evaporation, contacts were deposited. After deposition, the device was annealed at 425°C for five minutes.

The properties of the Co₃O₄ and CuO nanoparticles were analyzed using scanning electron microscopy (SEM) (TESCAN MIRA3, France). X-ray diffraction (XRD) analysis was performed with a Phillips PANalytical X'pert

diffractometer (Holland). The optical characteristics of the deposited films were recorded using a UV-Vis spectrometer (Shimadzu, UV-3600) at room temperature. The metal-semiconductor-metal (MSM) photodetector consisted of two interdigitated electrodes, each with four fingers. Each finger had dimensions of 230 μm in width, 3.3 mm in length, and 400 μm in separation. Aluminum (Al) contacts were fabricated using vacuum thermal evaporation with a metal mask, which was patterned according to the contact structure.

The spectral UV photoresponse of the fabricated Co₃O₄ photodetector was measured using a monochromator with a 150 W xenon lamp as the UV light source. A Keithley 2400 source meter was employed to measure the photocurrent. The system was controlled by a PC using LABVIEW via a GPIB interface. All measurements were performed under ambient conditions (temperature: 25°C, humidity: 62%).

3. RESULTS AND DISCUSSION

The morphology of the grown CuO and Co₃O₄ on quartz, as well as on the produced CuO, is shown in Fig. 1(a and b). It is clearly observed that the CuO nanostructures, formed by the thermal evaporation of metal copper through a vapor-solid (VS) mechanism, were successfully fabricated. The resulting copper oxide thin film was then used as a substrate for growing the crystal-like Co₃O₄ nanostructures, as shown in Fig. 1(b). The surface morphology of the Co₃O₄ nanostructures reveals nanocrystal-like particles. The growth of the Co₃O₄ film was controlled by nucleation, which occurred first, followed by crystal growth from the crystal nuclei. The possible growth mechanism of the crystal-like Co₃O₄ nanostructures is strongly influenced by plasma dynamics, surface interactions, and oxygen partial pressure. The proposed mechanism is as follows: first, after the high-energy pulsed laser strikes a Co₃O₄ target, it leads to forms a plasma plume of Co, Co₃O₄, and oxygen species, the Co₃O₄ species in the plasma adsorb onto the high surface energy and potential defects CuO which is act as preferred nucleation sites. Due to high temperature (700°C), Co₃O₄ atoms have enough energy to diffuse and rearrange into well-defined crystal-like nanostructures. This result indicates that the Co₃O₄ nanostructures had a high quality with a clear and distinctive form of a crystal-like structure.

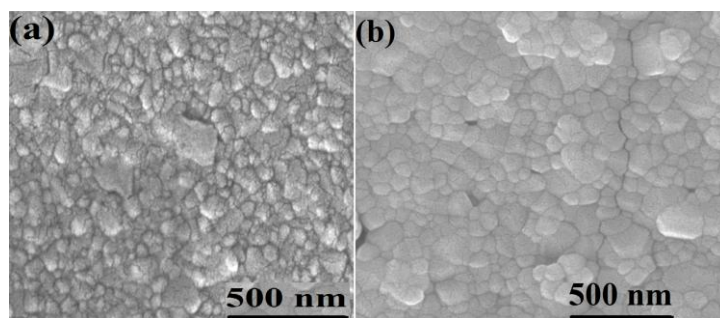


Figure 1. FESEM images of (a) CuO on Quartz substrate and (b) crystal-like Co_3O_4 nanostructures grown on CuO/Quartz substrate.

The crystal quality and orientation of the grown CuO thin film on quartz and crystal-like Co_3O_4 on CuO /quartz substrate were analyzed by XRD. Figure. 2 a,b shows the obtained XRD patterns of grown CuO thin film and crystal-like Co_3O_4 on quartz and CuO/quartz substrates, respectively. The obtained diffraction peaks can be related to crystalline CuO with Monoclinic structure, which agrees with the ICDD Card Number: 01-080-1916 for CuO [17] with peaks Characteristic peaks at $\sim 32.5^\circ$, 35.5° , 38.7° , 48.8° , 53.4° , 58.3° , 61.6° , 66.1° , 68.0° . The detected XRD peaks of

crystal-like Co_3O_4 nanostructure with the standard diffraction patterns of cubic Co_3O_4 and showed sharp and more intense peaks at peaks at 36.5° , 42.4° , 61.5° , 73.9° , 77.3° . The narrow full width at half maximum of those peaks indicates the good crystallinity of the grown crystal-like Co_3O_4 . This also reveals the interface architecture in eliminating the effect of amorphous SiO_2 layer. It is clear from comparing these results with those on other substrates the importance of CuO layer and how crucial it is to include the copper oxide interlayer.

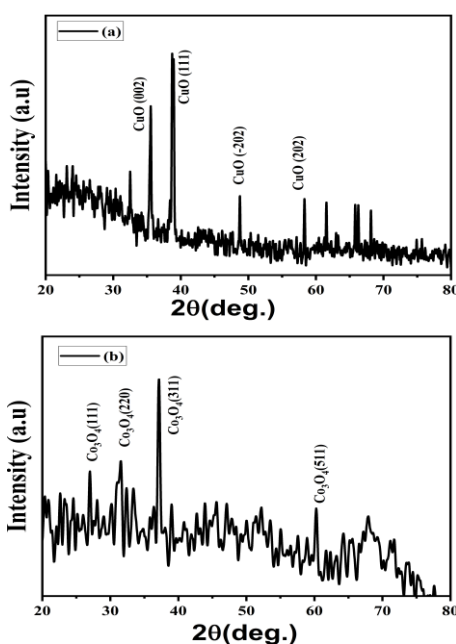


Figure 2. The XRD patterns of (a) CuO on Quartz substrate and (b) crystal-like Co_3O_4 nanostructures grown on CuO/Quartz substrate.

Using UV-Vis spectroscopy, the optical properties of CuO deposited on quartz were studied before and after the deposition of crystal-like Co_3O_4 nanostructures at 700°C . Figure 3 a,b shows the curve used to calculate the energy bandgap. It can be observed that there was a decrease in the bandgap value (1.87 eV) for crystal-like Co_3O_4 nanostructures. This distinctive feature was attributed to the recombination of free excitons in CoO, which leads to a reduction in the bandgap. Additionally, the decrease could also be attributed to the interfacial states introduced by the addition of crystal-like Co_3O_4 nanostructures to CuO. It is observed from the figure that the bandgap value of crystal-like Co_3O_4 nanostructures is shown in Figure 3 b. referred to

a near-band-edge (NBE) emission in the visible region at $\sim 660\text{ nm}$. generated by the recombination of the excitons through an exciton-exciton collision process. This value is attributed to the fact that the effect of CuO nanoparticle can either increase or decrease, depending on the specific conditions and properties of the CoO-CuO system. The linearity in the CoO curve is related to near-band-edge emission as well as the energy bandgap the curve does not exhibit any irregularities or deviations that could indicate the presence of defects or, resulted from high crystallization because the improvement of crystal quality could cause a linear near-band-edge emission with single tangent path.

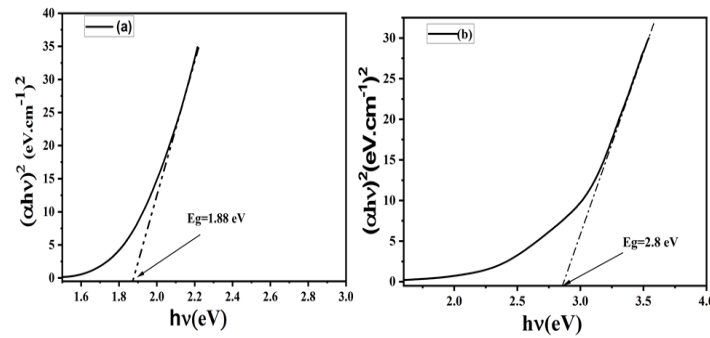


Figure 3. The UV-Visible spectra of (a) CuO on Quartz substrate and (b) crystal-like Co₃O₄ nanostructures grown on CuO/Quartz substrate.

Figure 4 shows the Current-voltage (I-V) characteristics of the fabricated Al-crystal-like CoO-Al MSM photodetectors PD operating in the dark (dark current) and under 450 nm illumination (photocurrent) while the incident optical power was 1.5 mW at room temperature. The low value of the dark current indicates minimal noise, which is desirable. The I-V characteristics of PD were measured for photocurrent and dark current of crystal-like CoO. The curve shows the photodetection activity is evident from the I-V curve. In addition to structural effect, the CuO substrate actively participates in charge transport. The measured

photocurrent to 450 nm light demonstrates that the crystal-like Co₃O₄ nanostructures /CuO interface promotes effective light-to-current conversion. At an applied bias voltage of 5 V, the dark current and photocurrent of the fabricated MSM photodetector were 8.14 μA and 442 μA, respectively. We observed the photo current of Al-crystal-like Co₃O₄ nanostructures -Al MSM was increase under 450 nm light, indicating that the photodetector has good response. A high photocurrent could be attributed to light-induced electron-hole generation at the depletion area of Al-crystal-like Co₃O₄ nanostructures -Al.

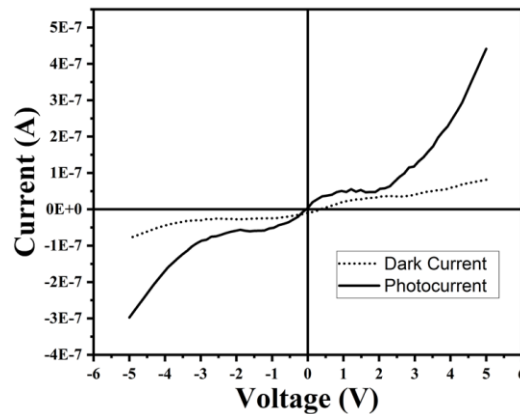


Figure 4. The I-V characteristics of the fabricated MSM photodiode measured in dark and under illumination of crystal-like Co₃O₄ nanostructures grown on CuO/Quartz substrate MSM photodetector.

For Al-crystal-like Co₃O₄ nanostructures-Al MSM PD, the response and recovery times are a very important factor for applications. The dependences of photocurrent on operating time for the Al-crystal-like Co₃O₄ nanostructures-Al MSM PD under visible light (450 nm) with power density of 1.5 mW/cm² at the bias of 5V is shown in Figure 5. Under 450

nm (turn on), we observed that the current of the PDs increases very slowly to reach saturation, and at turn off of the lamp, the current decreases also slowly. Also it is deduced the response time of the Al-crystal-like CoO-Al MSM PD to visible light was detected, the response and recovery times about 7.4 and 9.1 s respectively.

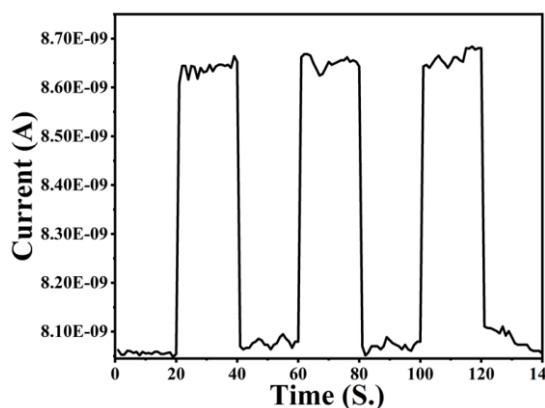


Figure 5. The photocurrent-time response of the (Al- crystal-like Co_3O_4 nanostructures -Al) photodetector measured under 5 V bias.

4. CONCLUSION

Crystal-like Co_3O_4 nanostructures were synthesized in two steps: first, by a simple thermal evaporation method to deposit copper oxide on quartz without catalysts or additives, and second, by pulsed laser deposition of Co_3O_4 onto the produced CuO. Morphological images of the deposited crystal-like Co_3O_4 indicated that the crystals uniformly covered the entire surface of the copper oxide and were uniformly shaped. X-ray diffraction (XRD) analysis confirmed that the formed product was cubic and exhibited the Co_3O_4 phase. The UV-visible spectroscopy at room temperature showed that the obtained Co_3O_4 nanostructures possessed good crystal quality with excellent optical properties. Moreover, the spectrum confirmed that the grown sample had a bandgap of 1.87 eV. The energy gap value for optical absorption indicating blue shift of absorption peaks relative to bulk Co_3O_4 .

The (Al- crystal-like Co_3O_4 nanostructures -Al) MSM photodetectors were then fabricated. I-V measurements revealed exceptional optoelectronic properties, the dark current and photocurrent of the fabricated MSM photodetector were $8.14 \mu\text{A}$ and $442 \mu\text{A}$, respectively, at a bias voltage of 5 V. These materials provide the basis for the design of advanced photodetectors.

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