Laser modification of Au–CuO–Au structures for improved electrical and electro-optical properties

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Abstract

CuO nanomaterials are one of the metal-oxides that received extensive investigations in recent years due to their versatility for applications in high-performance nano-devices. Tailoring the device performance through the engineering of properties in the CuO nanomaterials thus attracted lots of effort. In this paper, we show that nanosecond (ns) laser irradiation is effective in improving the electrical and optoelectrical properties in the copper oxide nanowires (CuO NWs). We find that ns laser irradiation can achieve joining between CuO NWs and interdigital gold electrodes. Meanwhile, the concentration and type of point defects in CuO can be controlled by ns laser irradiation as well. An increase in the concentration of defect centers, together with a reduction in the potential energy barrier at the Au/CuO interfaces due to laser irradiation increases electrical conductivity and enhances photo-conductivity. We demonstrate that the enhanced electrical and photo-conductivity achieved through ns laser irradiation can be beneficial for applications such as resistive switching and photo-detection.

Keywords: laser nanojoining, defect engineering, CuO nanowire devices, nanosecond laser, resistive switching, photocurrent, metal-semiconductor-metal structure

(Some figures may appear in colour only in the online journal)

1. Introduction

Metal oxide semiconductors such as titanium dioxide (TiO\textsubscript{2}), copper oxide (CuO) and zinc oxide (ZnO) are an important and broadly-studied class of semiconductors. An increasing demand for device miniaturization has focused attention on the nanoscale properties of these metal oxide semiconductors. Their nanomaterials have shown great potential in various applications such as photocatalysis [1–5], bio-sensors [6–9], and bio-medicine [10–13]. Due to the high surface-volume ratio and quantum-size effects in nanoscale systems, one-dimensional metal-oxide-semiconductor nanomaterials, including metal-oxide nanowires, have become essential building blocks in the construction and assembly of many nano-devices such as solar cells [14–18], photodetectors [19–23] gas sensors [24–28], and memristors [29–33]. To fabricate functional nano-devices, metal-oxide nanowires are often connected to metal electrodes to establish a metal-semiconductor-metal (MSM) nano-structure. It has been found that the electrical and mechanical characteristics of the contact region at the interface between metallic and semiconductor components can significantly influence the overall performance of these devices. For example, previous studies have shown...
that engineering the contact to introduce a Schottky barrier greatly improves the recovery time of an ultraviolet detector formulated with an MSM nanostructure [34, 35]. This process is facilitated in metal-oxide nanomaterials since the optical and electrical properties of these compositions are strongly dependent on the concentration of oxygen or metal vacancies [36–38]. The overall performance of nano-devices containing metal-oxide nanowires can then be engineered by controlling the type and concentration of defects within the metal-oxide nanowire. As a result, processing techniques that can tailor the mechanical and electrical properties of the metal-semiconductor interface and increase the defect concentration in metal-oxide nanomaterials show great potential to improve the performance of nano-devices. One of these emerging technologies involves plasmonic engineering at metal/semiconductor interfaces through exposure to femtosecond (fs) laser irradiation [39, 40]. Trapping of plasmons at metal/semiconductor interfaces has been found to result in the localized deposition of energy that can lead to metallurgical bonding at these interfaces, producing robust junctions and an improvement in the mechanical and electrical properties of the contacts. In addition, oxygen-deficient compositions can be formed within a few nanometers near junctions in these nano-devices, giving rise to enhanced conductivity [41]. However, previous studies exploiting plasmonic engineering at the interface only focused on n-type semiconductors whose conduction depends mostly on the oxygen vacancies, while p-type conductivity often depends on defects such as metal vacancies. Whether laser irradiation can modify the type and the concentration of such defects in p-type semiconductors and how this process may be useful for tailoring the p-type conductivity and photo-conductivity remained unknown. As one of the representative metal-oxide semiconductors with medium bandgap energy, CuO and its one-dimensional nanomaterials, have been widely studied due to low production cost and good suitability for applications in high-performance nano-devices [42–46].

In this work, we use nanosecond (ns) laser pulses to tailor the optoelectrical properties of MSM bridged structures consisting of CuO nanowires (CuO NWs) supported on interdigital gold electrodes. Nano-devices made of p-type semiconductors such as CuO often suffer from low current densities due to the relatively low mobility of holes [47]. Processing with ns laser pulses results in the formation of robust heterojunctions at Au/CuO interfaces, together with notable improvements in electrical conduction and mechanical stability. In addition, laser irradiation of CuO NWs with ns pulses has been found to affect the concentration of point defects leading to significant changes in electrical and photoconductivities. To illustrate the capabilities of laser processing with ns pulses in CuO NW systems, we fabricate photodetectors based on MSM CuO bridged structures, and demonstrate the optoelectrical response of a light-assisted memristor incorporating laser engineered CuO NWs.

2. Experimental section

CuO nanowires were obtained by heating a clean copper foil (≥99.8%, 0.1 mm thick, Sigma-Aldrich) at 500 °C for 4 h in air. The CuO NWs were dispersed in ethanol (≥99.9%, Sigma-Aldrich) for storage. Their average diameter is around 100 nm with lengths ranging from 2 to 5 μm. Interdigital gold electrodes with a 2 μm finger spacing were fabricated on a SiO2/Si substrate using standard photolithography and lift-off techniques. Electrodes were first rinsed with high purity acetone (≥99.5%, Sigma-Aldrich) and isopropanol (≥99.5%, Sigma-Aldrich) then dried in flowing nitrogen gas before the deposition of CuO NWs. The solution containing CuO NWs was drop-cast on the gold electrodes and left to dry in the air. Samples containing suspended CuO NWs were identified using both optical microscopy (Olympus BX-51) and scanning electron microscopy (SEM, Zeiss FESEM 1530) subsequently. The electrical characteristics of samples with suspended CuO NWs were measured at room temperature using source measure units (SMUs) that connected to a parameter analyzer (Keithley 4200A-SCS). A blue light-emitting-diode (LED) with a wavelength of 460 nm was connected to a programmable DC power supply (Keithley Series 2200) to generate constant or intermittent blue light illumination with an intensity of 4.5 × 10−3 W cm−2 at the surface of the sample. The LED and the samples as well as the measuring units were contained in an enclosure during the measurement to minimize the disruptions from the environment (figure 1).
After determining the baseline of electrical characteristics and optoelectrical properties of the prepared samples, they were irradiated with 4-nanosecond (ns) pulses from a 1064 nm neodymium-doped yttrium aluminum garnet (Nd: YAG) ns laser operating at 30 Hz. The laser fluences used for processing ranged from 180 to 300 mJ cm\(^{-2}\). A half-wave plate/neutral density (ND) filter combination was used for control over polarization and laser power. A convex lens was also used to produce a beam spot with a 1.25 mm diameter on the sample surface. After laser irradiation, the electrical and optoelectrical properties were measured again with the same apparatus. The elemental composition, chemical bonding, and valence state of the atoms in CuO NWs before and after laser irradiation were determined by Raman spectroscopy (Renishaw micro-Raman spectrometer) with an excitation wavelength of 633 nm and x-ray photoelectron spectroscopy (XP, Thermo VG Microlab 350). The presence of defects was inferred from ultraviolet–visible spectroscopy (UV–Vis, Shimadzu UV-2501). The electric field distribution in the heterojunctions during irradiation was simulated using commercial software [Lumerical finite difference time domain (FDTD) software].

3. Results and discussion

Figures 2(a) and (b) show SEM images of Au/CuO NW/Au bridged structures after ns laser irradiation for 5 min at a fluence of 180 mJ cm\(^{-2}\) and 200 mJ cm\(^{-2}\), respectively. The polarization of the laser irradiation is indicated by the double arrow. In figure 2(a), some morphological changes (indicated by red arrows) emerged at the CuO/Au interface which indicates that bonding can occur at these regions. When the laser fluence increased to 200 mJ cm\(^{-2}\), significant balling appeared at the end of the CuO NW and enhanced bonding is evident at the CuO/Au interface, as shown in figure 2(b). An SEM image of the same CuO NW at a lower magnification is displayed in figure 2(c) and small globules can be seen at both ends of CuO NW, indicating that melting has occurred and bonding between the CuO NW and the Au electrode has been achieved at these locations. At a high laser fluence (300 mJ cm\(^{-2}\)), significant melting has occurred and the CuO NW is broken in several places (figure 2(d)). Since the pulse duration of the ns laser is long enough for the establishment of thermal equilibrium throughout the nanowire, a classical heating model predicts that global melting should occur along the entire nanowire [48, 49]. However, the localization of these globules indicates that the temperature is higher in specific regions. This behavior can be attributed to the excitation of surface plasmon resonances (SPRs) as reported elsewhere [50–53]. The localization of SPRs at the Au/CuO interface produces strong heating and melting near the point of contact. Similar localized effects can also be induced due to the formation of a laser-excited electron–hole gas in the CuO semiconductor [54, 55]. When semiconductor and metal components are in mutual contact or close proximity, much of the energy in the SPRs will be concentrated in the gap plasmon mode between the two components, resulting in localized heating within both materials adjacent to the gap [56–58]. This effect can be seen in FDTD simulations (figures 2(e) and (f)) of the electric field distribution close to the junction area between the Au electrode and the CuO NW. Figure 2(e) shows the electric field distribution when the end of the CuO NW is close to the edge of the Au electrode. The strongest electric field enhancements occur in the region close to the edge of the Au electrode as well as at the end of the CuO NW and these enhancements overlapped in this configuration. Figure 2(f) shows the distribution when the end of the CuO NW is 400 nm away from the edge of the Au electrode. The strongest electric field enhancements also occur in the region close to the edge of the Au electrode and at the end of the CuO NW but they became two separate regions in this configuration. This is consistent with previous studies which show that the strongest electric field enhancements always appear at the corners, edges, and extremities of nano-structures [59–62]. As a result, additional plasmonic heating can be expected in these regions, yielding higher temperatures and leading to the formation of globules as seen in the SEM images.

It is well established that point defects can be introduced into materials under high-intensity pulsed laser irradiation [63–67]. The spectroscopic properties of these defects are often obtained via UV–Vis absorbance spectroscopy. Figure 3(a) shows the normalized absorption spectrum before and after ns laser irradiation with 9000 pulses at a fluence of 200 mJ cm\(^{-2}\). It can be seen that the absorption edge has been extended from \(\sim 650\) to \(\sim 780\) nm after laser irradiation. This can be attributed to defect centers in the CuO NWs produced by laser irradiation. The bandgap energy can be extracted from a Tauc [51] plot as shown in figure 3(b) where the direct bandgap energy, \(E_g\), is obtained from an extrapolation of the linear plot of \((\alpha h \nu)^2\) versus \(h \nu\), where \(\alpha\) (cm\(^{-1}\)) is the optical absorption coefficient and \(h \nu\) (eV) is photon energy. This extrapolation shows that the bandgap energy changes from \(\sim 2.12\) eV in unirradiated CuO NWs to \(\sim 2.02\) eV after laser irradiation. A reduction in bandgap energy indicates that the presence of laser-induced defects is accompanied by the introduction of additional energy levels in the bandgap. A schematic showing the intermediate band introduced by defects and the corresponding interband transitions is given in figure 3(c). The existence of the intermediate band facilitates the absorption of photons with lower energies, which causes the redshift in the absorption spectrum. A variety of defect centers, including oxygen and copper vacancies as well as oxygen interstitials, are known to be present in intrinsic CuO NWs [68, 69]. The predominant defect is determined by the concentration of oxygen in the environment [70, 71]. Previous studies have shown that the formation energy of oxygen vacancies (\(\sim 3\) eV) is always much greater than that of copper vacancies (\(\sim 1.96\) eV) except in an oxygen-poor environment during equilibrium heating [70]. Since laser irradiation is carried out in an ambient air environment it is then possible that the dominant defects induced by ns laser irradiation are copper vacancies, although the strongly non-equilibrium excitation and heating/cooling conditions present during laser irradiation may result in the creation of oxygen vacancies.
The calculated change in the bandgap (0.1 eV) after ns laser irradiation is also close to the reported value (0.08 eV above the valance band) of the energy level of copper vacancies responsible for producing free holes [70]. The valence states of Cu in pristine and ns laser irradiated CuO NWs have been investigated by XPS. High-resolution XPS scans in the Cu 2p region before and after ns laser irradiation at a fluence of 200 mJ cm$^{-2}$ are shown in figures 3(d) and (e), respectively. In figure 3(d), the characteristic shake-up satellites near 943 eV are a clear indication that Cu$^{2+}$ is dominant in as-prepared CuO NWs [72, 73]. The double Cu$^{2+}$ satellite peak disappears, and the proportion of the shake-up peak compared to the main Cu 2p$_{3/2}$ peak at 934 eV is significantly reduced after laser irradiation, as shown in figure 3(e). This suggests that the concentration of Cu$^{2+}$ in the CuO NWs may have been reduced after irradiation. This effect could arise if irradiation introduces a copper-deficient phase although the laser-induced reduction of CuO to Cu$_2$O would also reduce the concentration of Cu$^{2+}$ [74]. To further investigate the compositional changes in CuO NWs produced by ns laser irradiation, we obtained Raman spectra of CuO NWs before and after laser irradiation (figure 4). The peak at 298 cm$^{-1}$, corresponding to the $A_g$ vibrational mode of CuO [58, 59], is clearly present in both spectra but becomes increasingly
asymmetric following ns laser irradiation. This asymmetry indicates that defect centers have been formed in the irradiation process [75, 76]. The appearance of the peaks at 149, 221, and 629 cm\(^{-1}\) can be attributed to the LO infrared mode \(G_{15}^{\text{LO}}\), the second-order overtone and one TO mode \(G_{15}^{\text{TO}}\) of Cu\(_2\)O [77, 78].

To study the influence of ns laser irradiation on the electrical conduction in the Au/CuO/Au bridged structure, \(I–V\) characteristics were measured using a voltage sweep from 15 to \(-15\) V under dark conditions. Figure 5(a) shows the \(I–V\) curve (with error bars) for the bridged structure containing a single nanowire before and after ns laser irradiation (200 mJ)
The inset is an expanded view of the low bias response. The shape of the I–V curve indicates a Schottky type Au/CuO contact formed. It is apparent that the overall conductivity was increased in both bias directions after ns laser irradiation. This is partly due to improvements in bonding at the Au/CuO interface, but changes in carrier concentration arising from laser-generated defects will also increase the conductivity. Before laser processing, the CuO NW was bonded to the Au electrodes by van der Waals forces, giving a weak mechanical contact and the gaps between the electrodes and the nanowire possibly exist. In this case, depletion regions at the contacting surfaces can be formed due to oxygen adsorbed on the nanowire surface [79, 80]. A potential barrier associated with a high concentration of adsorbed oxygen will therefore limit the current density passing through the contacts. Ns laser irradiation facilitates chemical bonding between Au and CuO and the formation of these metallurgical or covalent bonds will eliminate the adsorbed oxygen and result in a continuous structure [55]. The potential barrier is then reduced and charge transfer across the junction area is enhanced after ns laser irradiation. A previous study has shown that such variations in the height of the potential barrier can be inferred from the current amplitude in the low bias regime [81]. The inset in figure 5(a) shows that the current at low bias increases after ns laser irradiation, indicating that the potential barrier height has been lowered and the carrier concentration in CuO has increased after laser processing. Similar improvement in charge transport was also reported due to an increasing concentration of defects in CuO NWs [82]. To fabricate

Figure 4. Raman spectrum of CuO NWs before (black) and after (red) ns laser irradiation. The strongest peak at 298 cm⁻¹ corresponds to the Ag vibration of CuO while the weak peak at 150, 220, and 620 cm⁻¹ arises from Cu₂O.

Figure 5. I–V curves for the Au/CuO NW/Au bridged structure (a) consisting of a single nanowire and (b) three nanowires before (black) and after (red) ns laser irradiation with 9000 pulses at a fluence of 200 mJ cm⁻². The voltage sweep is 15 V → −15 V. The inset shows an expanded scale at low bias.
functional devices with reproducible performance and enhanced reliability, multiple CuO nanowires can be connected in parallel across the interdigital Au electrodes. Figure 5(b) shows I–V curves (with error bars) for a bridged structure containing three nanowires before and after ns laser irradiation. It can be seen that the current amplitude is significantly enhanced compared to that obtained in the single nanowire system. The overall improvement in response on laser processing is similar to that seen in the single nanowire case. This suggests that the Au/CuO NW/Ag configuration is scalable.

Since the bandgap of CuO corresponds to the energy range of visible light, there have been many studies on the use of this material as a photodetector. In recent years, attention has focused on the use of CuO NWs in such applications [83–86]. To investigate the role that ns laser irradiation might play in improving the optoelectrical properties of the bridged Au/CuO NW/Au structure, the photo-current was measured before and after laser processing (figure 6) using a blue LED (460 nm) as a light source. Figure 6(a) shows that both the dark current and the photo-current increase after ns laser irradiation. For instance, the dark current has been tripled and the photo-current has been doubled at a forward bias of 15 V after laser irradiation. The increase in dark current follows the data shown in figure 5(a), while the increase in photo-current can be attributed to the lowered potential barrier at the Au/CuO interfaces as well as to the introduction of energy levels due to defects close to the junction area. It has been reported that a lowered barrier height at the metal-semiconductor interface can facilitate the direct tunneling of photo-generated carriers across the junction [87]. Defects produced by ns laser irradiation near either of the Au/CuO interfaces can also introduce mid-gap states that liberate charge carriers on exposure to incident light [88] figure 6(b) shows the ON/OFF response of the photo-current at a bias of ∼15 V. It can be seen that both ON and OFF currents are increased by 8 nA, but that there is essentially no change in the signal-to-noise ratio following ns laser irradiation. In all cases, the photocurrent initially increases rapidly (∼0.1 s) upon illumination and then slowly increases towards saturation. A more robust photodetector, generating higher photocurrent, can be obtained by connecting multiple CuO NWs in parallel across the Au electrodes. Figures 6(c) and (d) display the current response for a bridged structure consisting of four CuO NWs. Figure 6(c) shows that the overall current amplitude for this system of multiple nanowires is ∼2 orders of magnitude larger than that of the single nanowire. However, the I–V response is more asymmetric because the response of each Au/CuO NW/Au component is not identical as many previous studies reported [43, 84, 89]. Changes in dark current and photo-current after ns laser irradiation are, however, consistent with that occurring in the single Au/CuO NW/Au system. Figure 6(d) shows the time response of the photocurrent at a reverse bias of 15 V, indicating that the difference
where detector, the responsivity, between photo-current and dark current has been tripled after ns laser irradiation.

To quantitively describe the performance of a photo-detector, the responsivity, \( R \), gain, \( G \), and detectivity, \( D \), were calculated as follows:[83]

\[
R = \frac{I_p - I_d}{P_{in}} = \left( \frac{q\lambda}{hc}\right)G
\]

\[
D = \frac{R \lambda^2}{(2qI_0)^2}
\]

where \( I_p \) is the photocurrent, \( I_d \) is dark current, \( P_{in} \) is incident light power, \( q \) is electron charge, \( \lambda \) is the incident light wavelength, \( h \) is Planck’s constant, \( c \) is the speed of light and \( A \) is the effective area that absorbs incident light. A summary of these parameters calculated for the different configurations in this work is given in table 1. These data indicate that all three characteristic parameters have improved after ns laser irradiation. For the single CuO NW configuration, the responsivity and the gain doubled meanwhile the detectivity is 1.4 times larger after ns laser irradiation. For the device consisting of four CuO NWs, all three parameters are one order of magnitude larger than the value in the single CuO NW case and ns laser irradiation further enhanced these values more than double. For comparison, table 1 also lists the data from other studies which employed CuO nanomaterials for photo-detection at similar wavelengths [21, 42, 90, 91].

Resistive switching in metal-oxide nanowires is another aspect of the electrical characteristics of these devices that has been the subject of many recent studies [92–96]. It is now generally accepted that resistive switching in metal oxides is due to the formation of internal conductive filaments. In this model, when a ‘SET’ voltage is applied, charged defects in the metal oxide assemble to form conductive filaments. This gives rise to the low resistance ‘ON’ state. Subsequent application of a reverse bias (the ‘RESET’ voltage) can ‘erase’ these conductive filaments and return the material back to a high resistance ‘OFF’ state. Defects in the metal oxide play a critical role and determine the detailed response involved in the resistive switching mechanism. To study the influence of ns laser irradiation on the resistive switching behavior of the present Au/CuO NW/Au bridged structure, \( I-V \) characteristics have been obtained using a cyclic voltage sweep. To avoid problems with joule heating and thermal runaway in a single bridged structure subjected to many voltage sweep cycles, which can lead to breakage in the NW or contact region [67], we have carried out these measurements using a bridged structure with seven CuO NWs. Figure 7(a) shows the current response during a voltage cycle \( 0 \text{V} \rightarrow 6 \text{V} \rightarrow -6 \text{V} \rightarrow 0 \text{V} \) for this bridged structure before and after ns laser irradiation with 9000 pulses at a fluence of 200 mJ cm\(^{-2}\). The resulting \( I-V \) curves exhibit the hysteresis typically seen in resistive switching devices. Before ns laser irradiation, the current response shows a typical Schottky characteristic with the applied bias increases from 0 to 3.1 V. The \( I-V \) curve is found to be linear in the voltage sweeps from 3.1 to 6 V followed by the sweep from 6 to 0 V. These characteristics can be attributed to the formation of conductive filaments due to the drift and accumulation of defect centers in the CuO NWs. Once the filaments are formed, the entire bridged structure transforms to a low resistance state (LRS) which is responsible for the linearity in the \( I-V \) curve. When the applied bias is reversed, the existing conductive filaments in the CuO NW will be erased and the entire structure returns to a high resistance state (HRS). After ns laser irradiation, the current increased significantly in both bias directions as expected because irradiation increases the conductivity of the bridged structure by introducing more defects in the nanowire as well as achieving better contacts between Au electrodes and CuO NWs. In addition, the onset of the linear part of the current response begins at a forward bias of 2.5 V rather than at 3.1 V in the unprocessed system. This indicates that the threshold for electroforming of the conductive filaments occurs at a lower bias voltage. This shift can be attributed to the presence of a higher concentration of defect centers following ns laser irradiation as well as to the lowering of the potential barrier at the CuO/Au junctions. The ON/OFF ratio, given by the relative amplitudes of the current in the HRS and LRS conditions at a specific bias, is barely changed by ns laser processing. Stability is another major concern in resistive switching devices and is best assessed by measuring the current response for multiple voltage sweep cycles. Figure 7(b) shows the current response for the bridged structure shown in figure 7(a) as the number of cycles is extended to 10. It is seen that the peak current under both forward and reverse bias fluctuates significantly due to fluctuations in the Au/CuO NW contacts and the intrinsic instability of conductive filaments under high current flow. Figure 7(c) shows the current response of the same structure

| Configurations | Wavelength (nm) | \( R \) (A·W\(^{-1}\)) | \( G \) | \( D \) (cm·Hz\(^{1/2}\)/W\(^{-1}\)) | References |
|----------------|----------------|----------------|----|----------------|----------------|
| Single CuO NW before laser irradiation | 460 | \( 3.5 \times 10^2 \) | \( 5.3 \times 10^2 \) | \( 3.5 \times 10^{11} \) | This work |
| Single CuO NW after laser irradiation | 460 | \( 7.0 \times 10^2 \) | \( 1.1 \times 10^3 \) | \( 5 \times 10^{11} \) | This work |
| Four CuO NWs before laser irradiation | 460 | \( 4.4 \times 10^3 \) | \( 6.6 \times 10^3 \) | \( 1.2 \times 10^{12} \) | This work |
| Four CuO NWs after laser irradiation | 460 | \( 1.3 \times 10^4 \) | \( 2.0 \times 10^3 \) | \( 2.5 \times 10^{12} \) | This work |
| Single CuO NW | 600 | \( 2 \times 10^2 \) | \( 3.95 \times 10^2 \) | \( 6.38 \times 10^{11} \) | [42] |
| Single CuO-Cu$_2$O core–shell NW | White light | \( 1.1 \times 10^3 \) | | | [90] |
| CuO thin film | White light | 15.3 | | | [21] |
| CuO thin film | 450 | \( 3.3 \times 10^{-4} \) | | \( 1.00047 \) | \( 2.03 \times 10^8 \) | [91] |
after ns laser irradiation and indicates that much of this instability has been eliminated. It is also apparent that the peak currents in both forward and reverse bias conditions are significantly increased after ns laser processing. Similar improvements have been observed in the previous study [40]. Many recent studies have shown that the resistive switching effect can be enhanced upon light illumination [97–100]. To investigate the influence of light illumination on the present bridged structure, the I–V characteristics have also been obtained using a cyclic voltage sweep while under constant illumination with blue light. Figure 7(d) shows the current response under illumination during a voltage cycle 0 V → 6 V → −6 V → 0 V for the same bridged structure consisting of seven CuO NWs mentioned above. The current response was measured both before and after ns laser irradiation with 9000 pulses at a fluence of 200 mJ cm−2. The corresponding I–V curves exhibit the typical hysteresis similar to figure 7(a) and the current amplitude in both HRS and LRS conditions has increased. However, the ON/OFF ratio under light illumination is not significantly changed from the ON/OFF ratio obtained under dark conditions. Figure 7(e) shows the first 10 cycles of the current response for the bridged structure under blue light illumination as shown in figure 7(d). It is clear that illumination with blue light has little effect on current fluctuations caused by the instability of conductive filaments.

Figure 7(f) shows the first 10 cycles of the current response for the same configuration after ns laser irradiation and indicates that stability has been improved. In addition, the peak currents under both forward and reverse bias conditions are almost doubled after ns laser processing.

To combine the enhanced electrical and optoelectrical properties, we demonstrate a light-assisted memristor that employs intermittent light illumination to further improve the ON/OFF ratio. Figure 8(a) shows the current response (with error bars) of the same bridged structure consisting of seven CuO NWs mentioned in the above context. The I–V characteristics were taken after ns laser irradiation to exploit the advantages we have shown previously such as improved stability and enhanced current amplitudes. Instead of sweeping in cycles continuously (0 V → 6 V → −6 V → 0 V), the voltage was kept at 6 V while the blue light was turned on to achieve an optical ‘SET’ process. The voltage was maintained at 6 V for five consecutive measurements to ensure that the photo-current became stable. The voltage was then swept back to 0 V and kept at this value for five consecutive measurements while the blue light was turned off. The voltage was then swept to −6 V and maintained at this value to obtain similar results in the reverse bias direction. It can be seen that the differences between the HRS and LRS are magnified compared to the hysteresis loop shown in figures 7(a) and 7(b).
Figure 8. (a) The current response of a bridged structure consisting of seven CuO NWs under cycled voltage sweeps (error bars are shown). The voltage first raises to 6 V and then maintains at 6 V for 5 consecutive measurements while the structure is illuminated with blue light. The voltage is then swept back to 0 V and kept at 0 V while the blue light was turned off. The subsequent voltage sweep repeated this process in the reversed bias direction. The sweep directions are as indicated by the black arrows on the corresponding HRS and LRS scans. (b) The long-term performance of the structure over 50 cycles at a 2 V read voltage. The black line shows the current in the HRS while the red line shows the current in the LRS under dark conditions. The blue line shows the current in LRS under the same condition as shown in (a).

(d). Figure 8(b) shows the long-term performance of the structure over 50 consecutive cycles at a 2 V read voltage. The black line shows the current for the HRS while the red line shows the current for the LRS under voltage sweeps 0 V → 6 V → −6 V → 0 V in the dark. In this case, the ON/OFF ratio is ∼2. On the other hand, for voltage sweeps as demonstrated in figure 8(a), the current for the LRS has been enhanced in the presence of blue light illumination. Under these conditions, the ON/OFF ratio increases to 6.

4. Conclusions

In this work, we have developed a new technique that utilizes ns laser irradiation to engineer the electrical and optoelectrical properties of a Au/CuO NW/Au bridged structure. Improvements in the operating characteristics of this device are obtained through tailoring of laser-induced heating to produce localized melting in the CuO NW and enhance bonding in the contact region between the Au electrode and the CuO NW. SEM images clearly showed that a continuous bond is formed at the Au/CuO interface under these conditions, which reduces the potential barrier between Au and CuO. The UV–vis spectrum, XPS results in the Cu 2p region, and Raman spectrum all showed that irradiation with intense ns pulses also produces additional defects in the CuO NW. These laser-induced defects introduce new energy levels to form an intermediate band so that the effective bandgap is narrowed. Due to the decrease in the interfacial barrier as well as the increase in the concentration of defects, the electrical conductivity is significantly increased in the bridged structure. This is accompanied by enhanced photo-conductivity, responsivity, and photo-detectivity. The I–V characteristics for resistive switching in the CuO NW were also improved due to an increase in the concentration of defects through ns laser irradiation. As a result, the electroforming of conductive filaments in the CuO NW is more readily achieved, and the stability of current under high voltage bias has been improved significantly. To take advantage of these improvements in electrical and optoelectrical properties, we show that laser processing enables the use of the Au/CuO/Au device as a light-assisted memristor with an enhanced ON/OFF ratio. In general, the use of ns laser irradiation has been shown to be effective in engineering the optoelectrical properties of this MSM bridged structure, suggesting that this technology may be promising in the development of nanodevices based on this structure.

Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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