Anodic copper oxide nanowire and nanopore arrays with mixed phase content: synthesis, characterization and optical limiting response

Piyush Kar1,2, Mohammed Khairy El-Tahlawy3, Yun Zhang, Mohammad Yassin, Najia Mahdi, Ryan Kisslinger, Ujwal K Thakur, Abdelrahman M Askar4, Robert Fedosejevs and Karthik Shankar2

Department of Electrical and Computer Engineering, University of Alberta, 9211-116 St, Edmonton, Alberta, T6G 1H9, Canada

1 These authors contributed equally.
2 Authors to whom any correspondence should be addressed.
3 E-mail: pkar1@ualberta.ca and kshankar@ualberta.ca

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Abstract

Thin films consisting of copper oxide nanowires (NWs) containing a mixture of copper oxide phases were formed by electrochemical anodization in de-ionized water (DI) and methanol based electrolytes. Well-defined arrays of vertical nanopores were obtained via anodization in ethylene glycol (EG)-based electrolytes. Optical absorption spectra revealed the electronic bandgap of the NWs formed in DI and methanol to be 2.50 eV, and that of nanopores formed in EG electrolytes to be 1.94 eV. The nanostructures were found to exhibit p-type conduction through Mott–Schottky analysis. The as-formed nanostructures exhibited two photon photoluminescence with lifetimes ranging between 200 and 1100 ps. They also displayed strong optical limiting in the form of a 25% decrease in optical transmission at 800 nm at a relatively low fluence of 0.1 J cm$^{-2}$ and an absolute transmittance $<50\%$ over the entire range of laser fluence values used in this study. The optical transmittance decreased from 40% at an incident Ti:sapphire laser fluence of 20 mJ cm$^{-2}$ to $\sim9\%$ when the fluence was increased to 700 mJ cm$^{-2}$. Furthermore, the damage threshold of 0.7 J cm$^{-2}$ compares favorably with advanced optical limiting materials such as gold-graphene composites and single-walled carbon nanotube composites even without further optimization of nanoscale morphology to maximize scattering. Therefore the nanostructures of mixed copper oxide films studied in this report are particularly promising as optical limiters for protecting low damage threshold ($<1$ J cm$^{-2}$) photonic devices and are an important addition to the narrow selection of optical limiting materials that are currently available.

1. Introduction

Research focus on copper oxide nanostructures for optical and electronic applications continues to grow and is aimed at process simplicity and scalability [1]. In contrast with vacuum deposition processes—electrochemical anodization processes are scalable, the process instrumentation cost is low, and it is relatively simple to adjust anodization conditions in order to allow tuning of nanoscale morphology as well as the semiconducting and optical properties of the resulting semiconductors. Therefore, anodically formed copper-based nanostructures are attracting increased attention [2–4]. The use of copper oxide nanostructures is motivated by the Earth abundance and relatively low price of copper, coupled with the high performance potential of copper oxide for several leading edge applications; these include semiconductor catalysis, solar photovoltaics and biosensing [5–9]. Another interesting application of copper oxides is their use as optical limiters. The only optical limiting applications for copper oxide nanostructures reported to date are in our recent work and in a few other reports that emphasized copper oxide nanospheres or thin films [3, 8, 10–13]. Therefore, towards a solution for
enhancement of optical limiting performance, we introduce copper oxide nanostructures formed under three different anodization conditions.

Optical-limiting materials are required to exhibit low transmission of light under exposure to high intensity pulsed-lasers without sustaining damage. While a number of materials exist that can provide optical attenuation for laser fluence values of 9 J cm$^{-2}$ and higher, optical limiting materials capable of protecting photonic devices against laser damage occurring at fluence values less than 1 J cm$^{-2}$ are much needed. Currently, the best performing materials in this regime are carbon nanotube suspensions which exhibit an optical limiting threshold of 0.9–1.1 J cm$^{-2}$ and a damage threshold of 1.5–3.5 J cm$^{-2}$ [14].

The damage threshold in vacuum deposited CuO thin films was reported to be 0.083 mJ cm$^{-2}$, which is a very low value and insufficient to protect most photonic devices from damage during their operation [10]. On the other hand, suspensions of hollow Cu$_2$O submicrometer spheres in ethanol were found to withstand laser damage up to an input fluence of 1 J cm$^{-2}$ [13]. Herein we report nanostructured thin films consisting of a mixture of Cu$_2$O and CuO that exhibit the onset of optical limiting at 0.02 J cm$^{-2}$, an optical limiting threshold of 0.4 J cm$^{-2}$ and a damage threshold of 0.7 J cm$^{-2}$. The transmission of light and susceptibility to damage are dependent on the scattering properties of copper oxide nanostructures, which in turn is a function of the morphology and therefore controllable by varying the anodization conditions [3]. Although anodization is a simple process requiring only a power supply and an appropriate electrolyte, challenges exist in the synthesis of the copper oxide nanostructures with desired properties because the morphology, crystalline phase content and lattice defect distribution vary with small variations in the anodization voltage and electrolyte chemistry [2].

We identified anodization conditions for forming nanowires (NWs) of mixed Cu$_2$O and CuO phases (with CuO as the major phase) by using low viscosity DI and methanol based electrolytes. Furthermore, we found anodization conditions for forming nanopores of Cu$_2$O as the majority phase by using a higher viscosity EG based electrolyte. We report our findings on the semiconducting and electrical properties via detailed characterization using x-ray diffraction (XRD), Raman spectroscopy, steady state and time-resolved photoluminescence (PL) spectroscopy, semiconductor-electrolyte interfacial analysis, and UV–vis spectroscopy. Tests on these hitherto unreported nanostructures reveal their enhanced optical limiting performance.

2. Experimental details

2.1. Formation of anodic copper oxide nanostructures

Copper oxide nanostructures were synthesized by anodization of copper sputter–coated on fluorine doped tin oxide glass. The thickness of sputtered copper was 500 nm and the sputtering was performed using a direct current magnetron sputtering system. The anodization electrolyte consisted of 2.5 M (aqueous) NaOH (2%, by volume) and 0.5 M (aqueous) (NH$_4$)$_2$S$_2$O$_8$ (2%, by volume). The reminder of the volume (96%) was either de-ionized water (DI), methanol or ethylene glycol (EG). DI anodized nanostructures were dipped in anhydrous methanol, and air dried thereafter, for conversion of any hydroxide to oxide. The inter-electrode distance in the anodization process was maintained at 1.5 cm, and anodization was carried out at constant voltage using a graphite cathode.

2.2. Characterization

The morphology of the copper oxide nanostructures was imaged using a field emission scanning electron microscope (FESEM). The crystalline phase content was analyzed using glancing angle XRD and also by Raman spectroscopy. Optical characterization was carried out using UV–vis and PL spectroscopy. 2-photon fluorescence measurements were performed by using a Zeiss LSM 510 NLO multi-photon microscope. The 2-photon excitation laser wavelength of 750 nm was generated from a Ti:sapphire source, and the emission window was set between 341 and 704 nm. Electrochemical measurements were carried out using a three-electrode electrochemical cell connected to a potentiostat. The electrochemical cell consisted of a saturated KCl Ag/AgCl reference electrode, a graphite counter electrode, and a 0.05 M aqueous NaOH electrolyte. Parafilm covering was applied to all parts of the samples except for a 0.375 cm$^2$ section.

2.3. Optical limiting experiments

Figure S1 is available online at stacks.iop.org/JPCO/1/045012/mmedia provides a schematic illustration of the experimental setup. Single 120 fs laser pulses from an 800 nm Ti:sapphire laser were used for the experiment. Glass slides were used to reflect part of the incident laser beam and part of the transmitted laser beam, after passing the copper oxide film, onto calibrated fast photodiodes 1 and 2 respectively. The copper oxide thin film sample was placed at the focus of a 80 cm focal length lens on an insertable mount which allowed easy removal to cross calibrate the photodiodes for 100% transmission. The beam spot was measured at the focal spot position.
using a CCD camera yielding a spot size of 130 μm in diameter (FWHM). The energy per pulse was calculated from the average power measured using a power meter, with the laser running at 1 kHz repetition rate. The energy per pulse was used to calibrate the photodiodes, so that the fluence could be calculated for every single shot. The incident fluence was varied by rotating the half wave plate which rotates the polarization of the input beam with the horizontal portion of the rotated electric field vector transmitted through polarizer. Values of the fluences on the samples were varied between 0 mJ cm−2 and 0.7 J cm−2. The photodiode PD1 thus gave the incident fluence on the film while the signal from the photodiode PD2 gave the transmitted pulse energy and thus relative transmission through the film. Both photodiodes had diffusers mounted on the input surface to make them insensitive to any minor variation in beam distribution from shot to shot.

3. Results and discussion

Copper sputtered on FTO was anodized in DI and methanol electrolytes to form copper oxide NWs, and anodized in EG-based electrolytes to form copper oxide nanopore arrays. The nanostructures formed by the three anodization conditions used in this study varied in morphology and optoelectronic properties. The recipe that we adopted yielded reproducible nanostructured morphologies. Optimal anodization voltages varied with electrolyte viscosity, and were 4, 6 and 20 V for DI water, methanol and EG based electrolytes, respectively. In all three electrolytes, we employed alkaline conditions and a strong oxidizing agent. Copper oxide forms by oxidation of copper, and the process is accelerated by use of the oxidant ammonium persulfate. Subsequently, conversion of copper oxide to copper hydroxide occurs which in turn nucleates and grows into NWs [15]. The applied anodization voltage accelerates this process. Dehydration of DI anodized copper hydroxide NWs occurs by dipping in methanol solution. In viscous electrolytes such as EG, the nucleation and growth processes of copper hydroxide are restricted due to stronger solvation of OH− ions by a dense three-dimensional network of hydrogen bonds and lower ionic mobilities. In addition, the presence of persulfate ions in the electrolyte results in pitting and pore formation in the copper oxide due to etching action resulting in the formation of nanowires instead of NWs. A schematic illustration of the mechanism is shown for electrolytes with low viscosity in figure 1(d) (left) and for more viscous electrolytes (i.e. EG) in figure 1(d) (right).

FESEM images of anodic copper oxide NWs formed using DI and methanol based electrolytes are shown in figures 1(a) and (b), respectively. A FESEM image of a nanopore array, formed using EG based electrolyte, is shown in figure 1(c). High aspect ratio NWs with an overall vertical orientation were obtained with DI water-based electrolyte at 4 V. Randomly oriented, low aspect ratio NWs that appear to be ellipsoidal in shape were obtained in methanol-based electrolytes at 6 V. Ordered arrays of nanowires were obtained in EG-based electrolytes at 20 V. The average length of DI water anodized NWs was ~1 μm while the width was ~10–50 nm. The average length and width of methanol anodized NWs were ~100 nm and ~40 nm, respectively. The average diameter of the nanowires formed in EG was ~20 nm.

XRD patterns, shown in figure 2(a), demonstrate the presence of copper oxides of four different stoichiometries via distinct peaks in the anodic copper oxides nanostructures. However, CuO phase dominates in the DI and methanol anodized nanostructures and Cu2O phase dominates in the EG anodized nanostructures. The type and proportion of the oxides varied with anodization conditions i.e. electrolyte and voltage. Methanol anodized copper oxide NWs exhibit intense CuO peaks at 35.57° (JCPDS PDF#01-070-6829) and at 53.52° (JCPDS PDF#98-000-0429). The XRD pattern of methanol anodized NWs also reveals other oxides of copper, namely Cu2O (200) at 42.51° (JCPDS PDF#98-000-0186) and Cu4O3 (JCPDS PDF#98-000-0346). The methanol anodized NWs, however, also exhibit a sharp and significantly intense peak of Cu(HCOO)(OH) at 41.21° (JCPDS PDF#01-074-6971). Cu(HCOO)(OH) may have been formed by oxidation of copper by formate ions, which may have been produced in the electrolyte by methanol oxidation [16, 17]. The most intense copper oxide phase in DI anodized nanostructures is CuO, which is evident from the CuO (002) reflection at 35.57° (JCPDS PDF#01-070-6829), although there is an overlap with the FTO peak. Other major copper oxide phases in the anodized NWs are Cu4O3 (420) at 40.80° (JCPDS PDF#04-007-0694), Cu2O (200) at 42.51° (JCPDS PDF#98-000-0186) and Cu4O3 (301) at 47.53° (JCPDS PDF#98-000-0346). The metastable Cu4O likely forms in the initial stages of copper oxidation and therefore it is rational to expect it to be predominantly present in the portion of the copper oxide film that is closer to FTO. Cu2O is the dominant phase in the EG anodized nanostructures, and that is evident from the intense Cu2O (200) reflection at 42.45° and Cu2O (111) reflection indicated by the peak at 36.67° (JCPDS PDF# 00-0186). In EG anodized nanowires, it is also evident that other copper oxide phases, namely Cu3O and Cu4O, are present. In addition to copper oxides, the EG anodized nanowires exhibit a weak peak of Cu(HCOO)(OH) at 32.75° (JCPDS PDF#01-074-6971), and a prominent peak of Cu(COOH)2·4H2O at 49.82° (JCPDS PDF#00-0062-0001). Cu(COOH)2·4H2O is likely to have been formed due to partial oxidation of EG to glycolic acid and subsequent reaction with copper [18].
Raman spectra for the copper oxide nanostructures are shown in figure 2(b), where a broad band was observed between 290 and 500 cm$^{-1}$ for DI anodized copper oxide NWs. The broad band consists of the Raman active $B_g$ mode of CuO peaks at 330, 350 and 618 cm$^{-1}$ [19–21]. Raman spectra of Cu$_2$O generally correspond to the Raman active $\Gamma_{25}$ phonon mode, and are found in peaks associated with the broad band at 515, 555 and 780 cm$^{-1}$ [22–24]. In contrast to DI water anodized nanostructures, EG and methanol anodized NWs do not exhibit a broad band but exhibit Cu$_2$O peaks at 555 and 780 cm$^{-1}$.

The optical spectra of copper oxide NWs (figure 3) formed in both DI-based and methanol-based electrolytes exhibit a dominant twin-peaked structure at 295 nm and 325 nm respectively together with a shoulder centered at ~430 nm, that are characteristic of certain solution-synthesized phase-pure Cu$_2$O micro- and nano-structures [25, 26]. This might be due to the presence of significant amount of the Cu$_2$O phase in the nanostructures, as evidenced by the Cu$_2$O (200) reflections in their XRD pattern. While Cu$_2$O and CuO nanostructures exhibit a large diversity in their optical spectra due to the effects of quantum confinement, surface capping ligands and impurities [24], the features seen in figure 3 did not resemble the optical spectra in any of the published reports on CuO nanostructures. The UV–vis spectra of copper oxide nanopores anodically formed in EG-based electrolytes (figure S3) show a broad absorption band centered at ca. 400 nm with minor crests and troughs. Figure S4 shows the Tauc plots derived from the UV–vis absorption spectra. From the Tauc plots, the bandgap was determined to be 1.94 eV for EG anodized nanopore arrays, and 2.50 eV for the DI and methanol anodized NWs. Electronic bandgap values for copper oxides vary with crystalline phase composition, grain size and lattice constant [27]. The bandgap values exhibited by the copper oxide nanostructures are close to that exhibited by p-type Cu$_2$O but may also be indicative of mixed phase content [27].

PL emission spectra for the copper oxide nanostructures, shown in figure 4(a), were collected at an excitation wavelength of 280 nm, and exhibit distinct peaks at 361, 380 and 425 nm. The peak at 361 nm is likely due to electron–hole recombination processes in free excitons in CuO, and the peak at 380 nm is due to band-edge emission of cupric oxide nanostructures [28–30]. We thus have an unusual situation where the features in the absorption spectra are indicative of Cu$_2$O nanostructures while the emission is mainly characteristic of CuO films and nanoparticles. This could be a signature of the excitation energy transfer from the higher bandgap
Cu$_2$O to the lower bandgap CuO due to the formation of a Type-I (straddling) heterojunction between Cu$_2$O and CuO in the anodically formed NWs instead of the more commonly observed Type-II (staggered) heterojunction [31]. We attribute the weaker emission peak at 425 nm to defect-mediated recombination of electron–hole pairs originating in lattice defects and surface trap sites. Such defects tend to harden the crystal lattices, which may be a cause of superior nonlinear optical limiting performance (discussed later in the article). PL lifetime measurements of the copper oxide nanostructures were carried out with an incident 2-photon laser wavelength of 750 nm, and with an emission window set between 341 and 704 nm. The PL lifetime (figure 4(b) and inset) plots show contrast with respect to nanostructure type. The lifetimes plots have two regions: one is characterized by high intensities and short lifetimes and the other by lower intensities and longer lifetimes (as shown in the inset). As obtained from the lower intensities region, the mean fluorescence lifetimes are 228, 279 and 1079 ps for EG anodized nanopores, DI anodized NWs and methanol anodized NWs respectively. Figures 4(c)–(f) are the 2-photon images. The observed lifetimes are similar to those measured for CuO nanoparticles [32, 33] providing further support for the hypothesis that emission results predominantly from the CuO phase in mixed phase copper oxide nanostructures. NWs and nanopores exhibit distinct photoluminescence, while no PL was observed for the bare FTO under identical conditions.

Mott–Schottky plots for the copper oxide nanostructures are shown in figure 5, and reveal predominantly p-type character of the nanostructures that also imply Cu$_2$O as the majority crystalline phase. Charge carrier concentrations—obtained from the slope of the linear fits shown in plots by using the Mott–Schottky’s equation and by assuming a dielectric constant of 7.6 for Cu$_2$O—are of the order of $10^{15}$ cm$^{-3}$ for the EG anodized nanopores, and of the order of $10^{18}$ cm$^{-3}$ for the DI and methanol anodized NWs.
Nonlinear optical limiting data (i.e. fluence versus transmittance plots) are shown in figure S5 and in figure 6. To be certain that the optical limiting nonlinearity derives only from the copper oxide nanostructures, a blank microscope glass slide and a bare FTO substrate were tested with the same measurement procedure. The experiment was carried out on the samples using low to medium level fluences (up to 0.7 J cm\(^{-2}\)). The nonlinear transmission could be easily observed and repeated, as shown in figure 6. A distinct reduction in transmission was observed starting at around 20 mJ cm\(^{-2}\) and was repeatable at the same sample spot for three scans. The nonlinear absorption for a FTO substrate slide is also shown in figure S5, where it is observed that the fall off in transmission starts at about 20 mJ cm\(^{-2}\). However, the copper oxide nanostructures were located on the beam...
entrance side (see figure S1) of the FTO substrate and therefore the fluence transmitted through the film (much reduced from the incident fluence) subsequently interacted with the FTO film. As an example, at an incident fluence of 100 mJ cm\(^{-2}\), the transmission through the nanostructures will be less than 40% and therefore the expected transmission of the FTO substrate will be over 88%. Therefore, the drop in transmission observed for the copper oxide nanostructures occurs primarily within the nanostructures.

Figure 6 shows an expanded view of the plot shown in figure S5, corrected for 88% transmission loss by FTO, wherein it is demonstrated that the EG anodized nanopores, in spite of exhibiting a small-diameter (∼20 nm) nanopore structure that is non-ideal for Mie scattering, and a low free carrier density (\(N_D \sim 10^{18} \text{ cm}^{-3}\)), still exhibit a strong optical limiting effect, manifested in reduction of transmission from 47% at 0.02 J cm\(^{-2}\) to 19% at 0.7 J cm\(^{-2}\), which we attribute to excitonic absorption from large-radius and strongly bound Wannier excitons at high light intensities. Methanol and DI anodized copper oxide NWs show high nonlinear extinction that may be partially explained by the higher scattering expected from the NWs since one of their dimensions (i.e. their length) extends into several micrometers, which is a conducive size regime for Mie scattering. Contributions from excitonic and free electron (\(N_D \sim 10^{18} \text{ cm}^{-3}\)) absorption are also expected to be present. It is the convergence of scattering, excitonic and free electron absorption phenomena that render copper oxide nanostructures with at least one dimension in the micrometer- or submicrometer range, as highly promising materials for optical limiting applications.

4. Conclusion

High aspect ratio anodic copper oxide NWs were obtained using DI water based electrolyte. Low aspect ratio copper oxide NWs, appearing like nano-leaves, were obtained using methanol based electrolyte. Nanopore arrays of copper oxide were formed using EG based electrolyte. XRD and Raman results show the presence of mixed
CuO and Cu$_2$O phases in the nanostructures. Electronic bandgaps, obtained using UV–vis data, were close to 2.50 eV for NWs formed using water and methanol electrolytes, and 1.94 eV for nanopores formed using EG electrolyte. The nanostructures were fluorescent with lifetimes ranging between 200 and 1100 ps. The p-type nature of the anodic copper oxide nanostructures was revealed from Mott–Schottky plots. The simplicity of formation of these anodic copper oxide nanostructures (NWs and nanopores) serves as basis of further research towards their scalability and applications in other fields.

The optical limiting effect of the nanostructures could clearly be observed at fluences above 20 mJ cm$^{-2}$ using 120 fs 800 nm laser pulses. A reduction in transmission from 40% to between 9% and 18% was observed as fluence was increased from 20 to 700 mJ cm$^{-2}$. Optical-limiting properties of these anodic copper oxide nanostructures will serve as a benchmark towards formation of robust optical limiters, particularly for the protection of photonic devices that experience laser damage at a relatively low threshold fluence.

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ORCID iDs

Abdelrahman M Askar  https://orcid.org/0000-0002-6092-0031
Karthik Shankar  https://orcid.org/0000-0001-7347-3333

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