Three-dimensional (3D) ZnO–CuO core-shell nanorod arrays have been synthesized by a three-step process on silicon (100) substrates. A hydrothermal method was used to grow 3D ZnO nanorod arrays, followed by deposition of Cu nanofilm using sputtering, which was oxidized subsequently at 400 °C to form CuO shell surrounding ZnO nanorod core. The control over oxygen flow and pressure during the Cu nanofilm oxidation was found to improve the uniformity and intactness of CuO shell surrounding ZnO nanorod core. With higher oxygen flow, more conformal CuO thin film coating was achieved on the 3D ZnO nanorods array as a result of more sufficient oxygen access at the bottom portion of ZnO nanorods array. Higher pressure during thermal oxidation favored the formation of non-conformal ZnO–CuO core-shell nanorods and impurity Zn2SiO4 possibly at the interface of ZnO and Si substrate.

UV-vis absorption spectroscopy revealed higher absorption efficiency in the visible region in ZnO–CuO core-shell nanorods than in pure ZnO nanorods. The fabricated ZnO–CuO core-shell nanorods could be useful nanoscale building blocks in solar cells and light emitting devices.

**Introduction**

ZnO is an n-type semiconductor with direct band gap of ~3.3 eV at 300 K and large exciton binding energy of 60 meV, which makes it a promising optoelectronic and UV-emitting material. However, formation of p-type ZnO semiconductor is still a challenge because of its asymmetry doping. Recently, the effect of alloying on ZnO based nanostructures has drawn much attention because of their potential to improve electrical, optical and other functional properties. When interfaced with metal oxides or metals such as Co, Cu, MgO, and (La,Sr)CoO3 by alloying or doping, ZnO could find potential applications in photodetectors, light emission diodes (LEDs) and solar cells.

Amongst those metal oxides, copper oxide is a typical one with two polymorphs: Cu2O and CuO, both of which are p-type semiconductors, with direct band gaps of 2.0 eV and 1.2 eV, respectively. It has been found that when Cu2O is interfaced with ZnO, the formed Cu2O–ZnO p-n junction can be utilized in solar cells and gas sensor applications. However, the demonstrated energy conversion efficiency in Cu2O–ZnO p-n junction so far is low due to rather poor crystal quality and non-conformal characteristic of Cu2O layer on ZnO nanorods. Also, it is well documented that copper can be easily oxidized into either CuO or Cu2O and depending on different oxidative environments, distinct structures and morphologies can be achieved. It is worth noting that previous research mostly focused on oxidation behavior in 2D flat thin film or bulk Cu, while thermal oxidation of Cu nanofilm has been rarely studied on 3D nanoscale geometry, especially on nanorod case. Here, we report a successful fabrication of ZnO–CuO core-shell nanorod arrays by a three-step sequential method to improve the crystal quality and conformal characteristic of CuO shell during thermal oxidation process. We also investigated copper thin film oxidation behavior on 3D geometry of ZnO nanorod arrays under different growth conditions, mainly focusing on the effects of oxygen flow and pressure.

**Experimental**

In this study, 3D ZnO–CuO core-shell nanorod arrays were grown on Si (100) substrates by a three-step process: i) hydrothermal synthesis of ZnO nanorod arrays; ii) Cu nanofilm deposition using sputtering; and iii) thermal oxidation of Cu nanofilm. A 50 nm ZnO thin film layer was first deposited on a Si substrate by RF magnetron sputtering as a seed layer for ZnO nanorod growth, during which argon was used as carrier gas, and the deposition base pressure was controlled at ~5 × 10⁻³ torr. After annealing the seeded Si substrate at 200 °C for 30 min, ZnO nanorod arrays were grown by a hydrothermal method. In the hydrothermal process, zinc nitrate (Zn(NO3)₂·6H2O) and hexamethylenetetramine (C6H12N4, HMT) were used as precursors dissolved in deionized (DI) water with a 1 : 1 molar ratio (10mM). The ZnO seeded substrate was incubated in the solution at 80 °C for 4 h and then removed and rinsed in DI water and baked at 80 °C on hot plate overnight. A DC magnetron sputter was used to deposit a 20 nm Cu nanofilm onto the as-grown 3D ZnO nanorod arrays with argon as carrier gas, and a deposition base pressure of ~1 × 10⁻² torr. Finally, ZnO–CuO core-shell
nanorod arrays were formed by thermally annealing ZnO–Cu nanorod arrays with and without oxygen flow in the tube furnace for 30–60 min, with different flow rate and pressure control. To characterize the morphology, structure, and optical property of the grown nanostructures, a JEOL 6335F field emission scanning electron microscope (FESEM) attached with an energy-dispersive X-ray spectrometer (EDXS) attached, a FEI Tecnai T12 transmission electron microscope (TEM), a BRUKER AXS D5005 (Cu-K\textsubscript{α} radiation, λ = 1.540 598 Å) X-ray diffractometer (XRD), and a Cary 5000 UV-visible spectrometer were used.

**Results and discussion**

Fig. 1(a) shows a typical top view SEM image of the as-grown ZnO nanorods on a 50nm ZnO-seeded Si (100) substrate after hydrothermal process. Densely packed and uniformly aligned ZnO nanorod arrays have been fabricated with a diameter of ~80–100 nm, and a length of ~500–1000 nm on the substrate, as revealed by 30° tilt view SEM image shown in the inset. After a 20nm Cu sputtering deposition on 3D ZnO nanorod arrays, the nanorod diameter became ~100–120 nm, while the resulted ZnO–Cu core-shell nanorods retained their shape, as revealed in Fig. 1(b). The gap between adjacent ZnO–Cu nanorods is ~10–50 nm and 45° tilt view SEM image and the TEM image shown in the upper right inset of Fig. 1(b) suggests that Cu has been deposited onto ZnO nanorods as a ‘nanofilms’, leading to a nail-shaped nanorod. EDX spectrum analysis revealed ~16.27 at.% of Cu present in the top portion of ZnO–Cu nanorods, while drastically decreased Cu content of ~6.91 at.% in the bottom portion of ZnO–Cu nanorods. This further suggests that Cu intends to accumulate on top of ZnO nanorods resulting in the nail-shaped core-shell structure.

To convert the ZnO–Cu nail-shaped core-shell nanorod arrays into ZnO–CuO core-shell nanorod arrays, ambient oxidation at 400 °C was carried out for 1 h, which, however, turned into nearly solid ‘flat’ film on ZnO nanorod arrays as shown in Fig. 1 (c). The formed film was confirmed as CuO by EDX and X-ray diffraction analyses which are consistent with the recent report.\textsuperscript{\textsuperscript{17}} With the small gap of 10–50 nm between adjacent ZnO–Cu nanorods, it is likely that rapid oxidation process happened in ambient condition (1 bar), leading to a quick outward top surface oxidation with enough oxide film fill in the nanorod gaps. To avoid the fast oxidation process and improve the conformality of CuO film formation on the 3D nanorod arrays, a systematic study of the low pressure (<1 bar) and oxygen flow rate dependence has been carried out on the thermal oxidation behavior of Cu nanofilm on the 3D ZnO nanorod arrays. The Table I summarizes the various investigated samples after different thermal oxidation treatments.

Fig. 2 shows a set of comparative top-view SEM images of ZnO–CuO core-shell nanorods formed under different oxidizing conditions, with (a), (b), (c), (d) and (e) corresponding to samples S0, S1, S2, S3 and S4, respectively. The comparison of these top view images suggested that with increasing oxygen flow rate, thin-film like Cu\textsubscript{x}O morphology is more likely to form surrounding ZnO nanorods. Early studies have suggested that variation of oxygen partial pressure during thermal oxidation could affect the morphology of copper oxide film.\textsuperscript{\textsuperscript{26–27}} In our case, samples S1, S2, and S3 are formed under the same control of pressure and temperature (100 mbar and 400 °C). Therefore, oxygen partial pressure should be same in the tube furnace according to ideal gas law PV = nRT, where P = pressure, V = volume, n = amount of substance, R = gas constant and T = temperature.

In sample S4 annealed under 500 mbar, the oxygen partial pressure was higher than other samples, leading to nearly ‘flat’ Cu\textsubscript{x}O nanofilm morphology on top of ZnO nanorod arrays, as shown in Fig. 2(e), similar to the ambient oxidation result in Fig. 1(c). A 30° tilt view SEM image displayed in the inset further revealed non-conformal coverage of Cu\textsubscript{x}O nanofilm throughout the entire ZnO nanorod arrays. In this case, due to large oxidation rate at high pressure, fast Cu\textsubscript{x}O substances fill-in occurs between adjacent ZnO–Cu nanorods, leading to drastically increasing barrier of the oxygen diffusion from the top portion to the bottom portion of nanorod arrays. This will lead to the dominant upward (↑) oxidation of Cu film, forming a relatively flat CuO nanofilm on top of ZnO nanorod arrays.

To analyze the structure variation after thermal oxidation, XRD and TEM analyses were conducted. Fig. 3 shows the typical XRD spectra corresponding to samples under different conditions. Spectrum (a) from the as-grown ZnO nanorods shows a strong peak at 34.8° that corresponds to (0002) plane of wurtzite ZnO (JCPD 89-0511, Hexagonal, a = 3.249, c = 5.205) as a result of the nanorods’ preferential growth direction along [0001].\textsuperscript{\textsuperscript{28}} Spectrum (b) reveals the Cu peak at 43.3° that corresponds to (111) plane of Cu (JCPD 04-0836, Cubic, a = 3.615), which proves the successful deposition of Cu onto ZnO.
nanorods. Spectra (c), (d) and (e) display the XRD spectra from samples S0, S2 and S4. It is clear that all three spectra contain a common major peak at 34.8° corresponding to (0002) peak of ZnO nanorods, suggesting intact ZnO nanorod cores in the ZnO–CuO core-shell nanorods after various thermal oxidation processes. Spectra (c) and (d) show two broad peaks at 35.5° and 38.8°, which correspond to CuO (002)/(−111) and (111)/(002) planes (JCPD 89-5899, Monoclinic, \(a = 4.689\), \(b = 3.42\), \(c = 5.13\), \(\beta = 99.57\)), respectively. The broadening of peaks might result from nano-sized CuO crystallites. Also, the intensity of these two peaks tends to be much stronger for the sample under oxygen flow (sample S2) than the sample without oxygen flow (sample S0), suggesting that oxygen flow might enhance the degree of oxidation.

Spectrum (e) shows the XRD pattern of the sample S4 treated under 500 mbar, a much higher pressure than the other samples. Two peaks at 33.9° and 36.4° were identified in this case, which corresponds to Zn 2SiO 4 (211) (JCPD 24-1969, Orthorhombic, \(a = 5.74\), \(b = 11.5\), \(c = 8.395\)) and Cu 2O (111) (JCPD 78-2076, Cubic, \(a = 4.267\)), respectively. It is suggested that Zn 2SiO 4 might form at the interface of ZnO and silicon substrate. On the other hand, the oxygen rich condition could favor the formation of CuO instead of Cu 2O, however, 3D nanoscale geometry effect might introduce a non-uniform distribution of O 2 partial pressure dependent on the local position, which may introduce non-homogeneous formation of oxides, i.e., a mixture of Cu 2O and CuO may form even at a high overall O 2 pressure on the top surface of nanorod arrays. While the formation of Zn 2SiO 4 may play a role to reduce the access of oxygen for copper oxidation, which could lead to the formation of CuO instead of Cu 2O under 500 mbar, as indicated in the spectrum (e) in Fig. 3. Further study along this line is still on-going, which will be reported in the near future.

### Table 1

A list of five typical ZnO–CuO core-shell nanorod array samples (S0, S1, S2, S3, and S4) formed after various thermal oxidation processes with different pressure and oxygen flow rate control.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Samples</th>
<th>Temperature (°C)</th>
<th>Pressure (mbar)</th>
<th>Oxygen flow (sccm)</th>
<th>Core-shell characteristic</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>S0</td>
<td>400</td>
<td>100</td>
<td>0</td>
<td>Poor/non-conformal (Fig. 2(a))</td>
</tr>
<tr>
<td></td>
<td>S1</td>
<td>400</td>
<td>100</td>
<td>20</td>
<td>Poor/non-conformal (Fig. 2(b))</td>
</tr>
<tr>
<td></td>
<td>S2</td>
<td>400</td>
<td>100</td>
<td>50</td>
<td>Good/conformal (Fig. 2(c))</td>
</tr>
<tr>
<td></td>
<td>S3</td>
<td>400</td>
<td>100</td>
<td>80</td>
<td>Ok/less-conformal (Fig. 2(d))</td>
</tr>
<tr>
<td></td>
<td>S4</td>
<td>400</td>
<td>500</td>
<td>50</td>
<td>Poor/non-conformal (Fig. 2(e))</td>
</tr>
</tbody>
</table>

Fig. 2 ZnO–CuO core-shell nanorods formed by annealing ZnO–Cu core-shell nanorod at 400 °C for 1 h with different pressure and oxygen flow rate. (a) Top view SEM image of sample S0: without oxygen flow and 100 mbar pressure. Inset showing distinction between tip and body region and their EDXS composition difference on the right showing higher copper concentration on the tip region. (b) Top view SEM image of sample S1: 20 sccm oxygen flow and 100 mbar pressure. (c) Top view SEM image of Sample S2: 50 sccm oxygen flow rate, 100 mbar pressure and has good-conformal coating of the shell layer compared to any other sample. (d) Top view SEM image of sample S3: 80 sccm oxygen flow rate and 100 mbar pressure. (e) Top view SEM image and inset of sample S4: 50 sccm oxygen flow rate and 500 mbar pressure.

Fig. 3 A set of X-ray diffraction spectra collected from different nanorod samples including ZnO nanorod arrays (NAs), ZnO–Cu NAs, S0, S2 and S4.
Early theory for the thermal oxidation of flat copper thin film suggested that with a thickness less than 40 nm, the following three steps occur sequentially to define the oxidation behavior of flat Cu nanofilm:33

i. Oxidant absorbed on the surface of oxide/metal.

ii. Due to good electron affinity of oxygen, electrons will diffuse through oxidant by tunneling effect or thermionic emission to form O–, which built up an electric field between Cu ion (Cu+ or Cu2+) and O ion (O– or O2–).

iii. Cu ion will migrate to meet oxygen ion to form the copper oxide film since copper diffuses much faster than oxygen.

As stated earlier, previous work on Cu oxidation mainly focused on flat 2D film subjected to uniform oxygen pressure, while in this study, 3D ZnO nanorod arrays could play an important geometrical effect on the copper oxidation behavior.

Fig. 4 is a set of TEM images and electron diffraction patterns comparing samples S2 and S0, treated with and without oxygen flow, respectively. Fig. 4(a) is comparison of the nanorod tip regions of samples S0 (left) and S2 (right), both of these are Cu-rich on tip region and diffraction patterns indicated in the inset corresponds to a monoclinic CuO phase. With oxygen flow (sample S2), the tip region CuO tends to become more polycrystalline instead of single crystalline as seen in the inset of Fig. 4(a) (right). Fig. 4(b) revealed a uniform bundle of conformal ZnO–CuO nanorods, indicating the successful fabrication of 3D nanorod arrays. Compared to sample S0 annealed without oxygen flow (Fig. 4(c)), sample S2 has a thicker CuO nanoshell at the body region of nanorods (Fig. 4(d)). With no oxygen flow in the thermal oxidation process and because of the dense packing distribution of ZnO–Cu nanorods in the array form, limited amount of oxygen could be accessed at the bottom portion of nanorods. Therefore, drastically more oxygen access on the nanorod top surface than the bottom portion will cause the formation of non-conformal ‘flat’ CuO nanofilm grown on ZnO nanorod arrays, as revealed in Fig. 1(c) for the ambient oxidation of ZnO–Cu core-shell nanorod arrays.

To understand the microscopic mechanism in unique Cu oxidation behavior on the 3D nanorod arrays, a simple electrical field model is proposed here. To simplify the geometry, the nail-shaped ZnO–Cu nanorod can be divided into two parts: top portion as semi-sphere and body portion as cylinder, between which a single copper ion is located at the boundary as schemed in Fig. 5(a).

If oxygen content is richer on the top portion (semi-sphere), the built-in upward (↑) electrical field (E1) will be...
stronger than the outward (→) electrical field in body portion (E2), which will result in a dominant copper ion’s diffusion upward instead of outward diffusion towards shell (Fig. 5(b)). When introducing oxygen flow, the difference between oxygen local partial pressure at the top of sample and the bottom of sample might be large enough to conquer the geometric diffusion barrier of oxygen caused by the unique 3D morphology. In this case, oxygen will then diffuse into the bottom as shown in Fig. 5(c), resulting in more oxidant permeating into the bottom portion of the nanorods, inducing better coverage of copper oxide film surrounding core ZnO nanorods.

The optical property of ZnO–CuO core-shell nanorod arrays has been characterized by UV-visible absorption spectroscopy. Since substrates with high absorption coefficient will hinder the information extraction of absorption spectrum corresponding to nanorod arrays, we investigated the absorption efficiency of ZnO–CuO core-shell structure nanorod arrays grown on quartz substrate instead of silicon and used a blank quartz substrate as reference. Fig. 6 shows the result of absorption spectrum before and after forming ZnO–CuO core-shell nanorod arrays. It is clearly indicated that the pure ZnO nanorods array has higher absorption efficiency from 200 nm to 380 nm and the absorbance drops dramatically in the visible and infrared region, which is consistent with the literatures.34 ZnO–CuO core-shell structured nanorods array clearly displays higher absorption efficiency in the visible range (~400–750 nm) as compared to pure ZnO nanorod arrays and have maximum absorption in the range of ~200–400 nm, which might be resulted from both ZnO nano-rods and band to band transition of CuO.35,36 Compared to ZnO–CuO nanorod array formed with oxygen flow, the nanorod array formed without oxygen flow seems to have a steeper decay in terms of longer wavelength light absorption, which might be induced by the non-conformal coating of CuO nanofilms on ZnO nanorods. In addition, ZnO–CuO core-shell nanorod arrays have shown two common broad peaks, respectively at 370 nm, as predicted from the ellipsometry data.37 and 420 nm, suggesting the possible success of CuO alloying onto ZnO nanorod arrays. Further study is needed to confirm this alloying process.

Conclusion

Large scale ZnO–CuO core-shell structured nanorod arrays have been successfully synthesized onto Si substrates by a three-step sequential growth process to improve the crystal quality and conformal shell layer characteristic. It is found that thermal oxidation behavior of Cu nanofilm on the 3D ZnO nanorod arrays can be tuned by controlling the oxygen flow rates and pressure. When introducing oxygen flow, the difference between oxygen local partial pressure at the top of sample and the bottom of sample could be large enough to conquer the geometric diffusion barrier of oxygen caused by the unique 3D morphology of ZnO nanorods and thus increasing oxygen flow rate might increase local partial oxygen pressure, resulting in better copper oxide shell coverage throughout each individual ZnO nanorod. Higher pressure might favor the formation of non-conformal ZnO–CuO core-shell nanorods and impurity Zn2SiO4 at the interface of ZnO and Si substrate. ZnO–CuO core-shell nanorod arrays have better absorption efficiency in the visible region compared to pure ZnO nanorod arrays, which suggests the good potential of ZnO–CuO core-shell nanorod arrays as nanoscale building blocks in solar cell and light emission devices.

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