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Abstract
In this research work, nanowires were grown on brass (Cu - 37.2 wt% Zn) substrate by thermal oxidation. The substrate was oxidized at temperatures ranging from 350 °C to 600 °C in the presence of varying concentrations of O₂ (1%–100%) in N₂ flown at a rate of 200 sccm. The oxidized brass surface was characterized by field emission scanning electron microscope equipped with energy dispersive x-ray spectroscopy and transmission electron microscope. Four different types of morphological variations such as thin, thick with branches, circular-flake and flat-cone shape nanostructures were observed during oxidation at different conditions. However, the prevalence of thin and thick morphology with branches was more prominent and found in all growth conditions. The length and diameter of the nanowires varied from 1 to 30 μm and 50 to 500 nm, respectively, whereas the length of the branches varied from 1 to 3 μm. The composition of the nanowires was ZnO possessing a hexagonal wurtzite structure. The selected area diffraction confirms that the nanowires grew along $\langle 1 \overline{1} 2 0 \rangle$ directions. Based on the results, a stress induced mechanism is proposed for the growth of ZnO nanowires on Cu - 37.2 wt% Zn substrate.

Keywords: ZnO nanowires, brass, thermal oxidation, growth mechanism, wurtzite

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

1. Introduction
Zinc oxide (ZnO) has direct band gap of 3.37 eV at 300 K and large exciton binding energy of 60 meV, which fueled and fanned research interest towards ZnO based devices [1–3]. Some of the opto-electronic and nano-electronic properties of ZnO overlap with GaN ($E_g \sim 3.4$ eV at 300 K), which possesses attractive optical, electrical and thermal properties [2, 4]. However, ZnO has some advantages over GaN such as it has simpler crystal growth technology and fair availability, which resulting in lower cost of ZnO based devices [2]. For this reason, a great deal of ZnO based research works have been carried out in various fields including UV lasers [1], photodetectors [5, 6], field emitters [7, 8], field effect transistors [9], gas sensors [10, 11], dye-sensitized solar cells [12], hydrogen storage devices [13], Li-ion batteries [14], nanogenerators [15–17], super capacitor [18], catalyst [19] and bio-medical [20] applications.

In the recent years, the synthesis of a rich family of zero-dimensional (0D), one-dimensional (1D), two-dimensional (2D), and three-dimensional (3D) ZnO based nanostructures has been demonstrated and well documented which provides numerous opportunities for researchers to explore their properties for potential applications. So far, nanoparticles [21], nanowires [1, 8, 22], nanorods [5, 10, 23], nanotubes [11], nanoneedles [19], nanofibers [24, 25], nanobelts [26–28], nanorings [29], nanocombs [30], nanosheets [14], nanowalls [31], tetrapods [18], hierarchical [32], and thin film [33] of ZnO have been synthesized by various innovative techniques such as hydrothermal [10, 29], electrospinning [11, 13], ultrasonic irradiation [34], sol-gel [35], chemical vapor deposition [19], thermal evaporation [36], aerosol [25], photo-polymerization [14], spray pyrolysis [37], pulsed laser deposition [38], RF sputtering [28], molecular beam epitaxy

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and solid-state chemical reaction [39]. Though a great variety of morphological variations of ZnO can be obtained by the above mentioned processes, which might be particularly suitable for some specific applications; these methods often associated with the problems of the removal of catalyst and template, tedious methodological procedure, poor adhesion with the underlying substrate, less scalability, and high equipment cost. An alternative strategy for growing of ZnO based nanostructures directly on metal substrates is by simply heating them in ambient or O₂ containing environment through thermal oxidation process [8, 27, 40–50]. This process is very simple (one step), highly scalable, efficient, and cheap which facilitates device fabrication. The resultant ZnO nanostructures are highly crystalline and pure, which do not require any further treatment. In principle, patterned ZnO nanowires based arrays created by this method can be electrically addressed by the supporting substrate electrodes for applications, such as field emitters and gas sensors [22, 27].

Normally thermal oxidation of metallic Zn for the growth of 1D ZnO nanostructures is carried out at temperatures ranging from 450 °C to 700 °C [40–46], whereas melting temperature of Zn is relatively low (419.5 °C). Therefore, oxidation of Zn for the growth of 1D ZnO nanostructures results in highly roughened surfaces [51]. To overcome this issue, oxidation of Zn carried out on different substrates, such as Si [47, 48], CdTe [43], and sapphire [50] in the presence of catalyst or ZnO as buffer layer. However, the difference in thermal expansion coefficient between the substrate and ZnO buffer layer causes deleterious effect on their interfacial adhesion [51]. Beside this, poor electrical conductivity of these substrates limits the applications of ZnO nanowires in opto-electronics and nano-electronics devices [22]. In addition, the pre-deposition of the catalyst or ZnO buffer layer increases the methodological complexity, introduce impurities, and influence the adhesion of ZnO nanostructures with the underlying substrates; thereby degrading the performance of the products [22].

To overcome these aforementioned difficulties, ZnO nanostructures can be grown on brass (Cu–Zn alloy) substrates instead of Zn [22, 51–53]. According to the Cu–Zn phase diagram [54], brass containing less than 40 wt% of Zn remains solid until ∼890 °C–900 °C. For this reason, oxidation of brass is beneficial for the growth of 1D ZnO nanostructures at high temperatures since brass is resistant towards high temperature deformation and capable of providing enough Zn species for the formation of ZnO nanostructures [22]. The advantages of this approach include easy manipulation, suitability for large-area production, and good adherence of 1D ZnO nanostructures with the substrate [7]. Natural adhesion and conductivity between 1D ZnO nanostructures and substrate showed some promising applications, such as field emission devices [22] and gas sensors [27].

Though many researchers focused on the growth of 1D ZnO nanostructures on metallic Zn by thermal oxidation [8, 27, 40–50], only a few reports on brass oxidation [22, 51–53]. Most of the research work on brass was carried out on α-brass, where the Zn content is less than 35 wt% [22, 51, 52]. In the literature, the effects of the presence of α-β phase in brass (containing 35–45 wt% Zn) on the growth of 1D ZnO nanostructures by thermal oxidation is not well addressed. Beside the compositions of brass, other growth parameters such as oxidation temperature and O₂ concentrations were not studied explicitly. There is a lack of information in terms of characterizing the oxide layers that form beneath the 1D ZnO nanostructures during oxidation of brass.

The growth mechanism of 1D ZnO nanostructures on brass by thermal oxidation is not well addressed. There are some key differences between the oxidation of metallic Zn and brass. For example, the formation of 1D ZnO nanostructures on metallic Zn substrates typically occurs at temperatures of 450 °C–700 °C [40–46] and it involves liquid and/or vapor phase of Zn as the melting point of Zn is 419.5 °C [51]. For this reason, the vapor–liquid–solid (VLS) [41] and vapor–solid (VS) [43, 49] mechanisms are usually invoked to understand the growth of 1D ZnO nanostructures on Zn. However, the growth of 1D ZnO nanostructures on brass does not involve any liquid or vapor phase as the melting point of brass (∼890 °C–900 °C) is significantly higher than the oxidation temperatures (300 °C–600 °C) [51]. This suggests a completely different growth mechanism that may operate during the formation of 1D ZnO nanostructures by thermal oxidation of brass, which has not been addressed clearly.

In this research article, brass wire containing 37.2 ± 0.9 wt% of Zn was thermally oxidized to obtain 1D ZnO nanostructures. The effects of oxidation temperature and concentration of O₂ on the growth of 1D ZnO nanostructures were studied thoroughly. In depth characterizations of the as-grown 1D ZnO nanostructures as well as oxide layers beneath the 1D nanostructures were carried out. The results demonstrate the involvement stress driven mechanism for the growth of 1D ZnO nanostructures on brass during thermal oxidation. Based on the findings, a mechanism is proposed for the growth of 1D ZnO nanostructures on brass substrates during thermal oxidation.

2. Experimental procedure

Brass wire (K9M2-081007, EDM-Tools (M) Sdn. Bhd.) having thickness of 200 μm was used in thermal oxidation without any cleaning. Prior to oxidation, the wire was examined in the longitudinal direction and in cross-sections under field emission scanning electron microscope (FESEM: Zeiss Ultra-60 FESEM) equipped with energy dispersive x-ray (EDX: EDAX-Genesis Utilities) spectroscope.

The thermal oxidation setup used in this research work has been described previously [55, 56]. A 5 cm long brass wire kept in an alumina boat which was placed inside the quartz tube of a horizontal tube furnace (Lindberg Blue M, TF5503A-1). To obtain the optimum operating temperatures for the growth of 1D nanostructures, the furnace was heated in ambient from room temperature to 350 °C–600 °C at a heating rate of 30 °C min⁻¹. The brass wires were oxidized for 4 h at the peak temperature and then cooled down to room temperature by opening the lid of furnace.
To obtain the optimum concentration of O₂ for the growth of 1D nanostructures, the quartz tube was connected with two gas cylinders through mass flow controllers (MFCs: Sierra, C100L-CM-NR-2-0V1-SV1-PV2-V1) and a gas mixture as shown in figure 1. One of the gas piping line (line 1) was connected to a pure N₂ cylinder (5 N purity), while another line (line 2) was connected to a pure O₂ cylinder (5N purity). By controlling the flow ratio from these cylinders using MFCs, the concentration of O₂ was varied from 1 to 100% in N₂ inside the quartz tube. The total flow rate of the gases was fixed to 200 sccm during oxidation if not mentioned otherwise. The gases were exhausted through other end of the quartz tube. Before ramping up the temperature of furnace, the quartz tube was sealed and appropriate gas mixture (1%–100% O₂ in N₂) was flown for 30 min to remove contaminants. After that the furnace was heated to optimum oxidation temperature at a heating rate of 30 °C min⁻¹ and then the brass wire was oxidized for 4 h at the peak temperature. After oxidation, the furnace was cooled down by opening the lid but gases were flowing inside the quartz tube.

After oxidation, the brass wires were mounted in epoxy and polished until 0.02 μm finishes using standard metallographic techniques. The oxidized and mounted samples were characterized under FESEM equipped with EDX spectroscopy. Figure 2(a) shows the FESEM image of the as-received brass wire. The diameter of the wire is 200 μm. EDX spectroscopy was carried out at 10 random spots on the brass wire and a typical result is shown in figure 2(b). Peaks of Cu, Zn, O and C are seen in the spectrum. The average wt% of Cu and Zn in the brass wire is 62.8 ± 0.9 wt% and 37.2 ± 0.9 wt%, respectively. A small amount of oxygen is observed in the EDX analysis which may be due to the formation of surface oxides. The O content is varied from 1.18 to 4.92 wt% at different spots and the average is 2.03 ± 1.09 wt%. The tiny C peak may be obtained from the conductive carbon tape, which was used to stick the wire with FESEM sample holder or from contaminants. For these reasons, the counts from O and C are omitted from the calculation during counting the average percentage of Cu and Zn in the wire. From this point forward, this brass wire will be represented as Cu-37.2%Zn.

The as-received brass wires were characterized to obtain the elemental composition. To optimize the growth of 1D nanostructures, the brass wires were oxidized for 4 h at different temperatures (350 °C–600 °C) in the presence of varying concentration of oxygen (1%–100%). The nanowires and the oxide layers beneath the nanowires were characterized by different techniques to observe the morphological variations and to obtain elemental composition and crystal structures. Based on the results, a mechanism for the growth of ZnO nanowires on brass during oxidation is presented.

3. Results and discussion

The morphological and compositional analysis of as-received brass wire was performed under FESEM equipped with EDX spectroscopy. Figure 2(a) shows the FESEM image of the as-received brass wire. The diameter of the wire is 200 μm. EDX spectroscopy was carried out at 10 random spots on the brass wire and a typical result is shown in figure 2(b). Peaks of Cu, Zn, O and C are seen in the spectrum. The average wt% of Cu and Zn in the brass wire is 62.8 ± 0.9 wt% and 37.2 ± 0.9 wt%, respectively. A small amount of oxygen is observed in the EDX analysis which may be due to the formation of surface oxides. The O content is varied from 1.18 to 4.92 wt% at different spots and the average is 2.03 ± 1.09 wt%. The tiny C peak may be obtained from the conductive carbon tape, which was used to stick the wire with FESEM sample holder or from contaminants. For these reasons, the counts from O and C are omitted from the calculation during counting the average percentage of Cu and Zn in the wire. From this point forward, this brass wire will be represented as Cu-37.2%Zn.

The as-received Cu-37.2%Zn wire were oxidized in ambient at temperatures ranging from 350 °C to 600 °C for
4 h. After oxidation the wire became gray white. The FESEM images of the wire after oxidation are shown in figure 3. The insets of figure 3 show the high magnification images taken from the sides to obtain the length of the nanowires. For oxidation temperature of 350 °C, the growth of short nanowires is seen all over the surface of brass having length of 1–2 μm (figure 3(a)). At 400 °C, mixture of long and short nanowires is seen on brass wire (figure 3(b)). The long nanowires are seen to be located in small islands having length up to 6 μm with white contrast. For the oxidation temperature of 450 °C, high coverage of long nanowires is seen all over the brass wire (figure 3(c)). The nanowires having length of up to 10 μm are originated from globular shaped particles. With further increase in temperature to 500 °C, the nanowires become shorter and the oxide scale exfoliates from the core of brass wire (figure 3(d)). Exfoliation is more severe for the brass wire oxidized at 550 °C–600 °C (figures 3(e)–(f)). The as-grown nanowires are also shorter for the oxidation temperatures of 550 °C–600 °C. So, from the results it is clear that 450 °C is the optimum temperature for the growth of nanowires on Cu-37.2%Zn wire.

Comparing to the results with Yuan et al [51], the optimum oxidation temperature for the growth of nanowires on Cu-30%Zn (α-brass) is 300 °C and the length of nanowires were only ~1 μm. With increasing temperatures, the coverage of nanowires were decreased on Cu-30%Zn substrate and no nanowires were observed at 600 °C [51]. On the other hand, Wang et al [52] obtained nanosheets, nanocombs in temperature range of 550 °C–650 °C on Cu-30%Zn (α-brass). However, in the present case, nanowires grow at all oxidation temperatures with higher coverage and lengths up to tens of micrometers.

According to the Cu–Zn phase diagram [54], Cu-30%Zn alloy primarily contains α-phase, where Zn is in solid solution in face centered cubic α-Cu. However, in the present work the brass alloy contains 37.2 wt% of Zn, which belongs in the α-β′ region in Cu–Zn phase diagram [54]. The presence of body
The average thermal expansion coefficient of brass and ZnO (α-axis thermal expansion coefficient) is \(19 \times 10^{-6} \text{K}^{-1}\) and \(2.9 \times 10^{-6} \text{K}^{-1}\), respectively [57]. Due to huge difference in thermal expansion coefficient, the brass core shrinks more than ZnO during cooling process. This might be the reason for the high rate of exfoliation at high oxidation temperatures. Beside this, the length of the nanowires becomes shorter at oxidation temperatures of \(500 \text{°C}\) and above. According to Cu–Zn phase diagram, the \(\beta\) phase in α–β brass transforms to β phase at \(458 \text{°C}\) [54]. The presence of β phase instead of \(\beta\) may be the reason for the growth of shorter nanowires at \(500 \text{°C}\) as seen in figure 3(d). However, with increasing temperatures to above \(500 \text{°C}\), the length and coverage of the nanowires starts to grow again (figures 3(d)–(f)).

For the determination of optimum concentration of oxygen for the growth of nanowires on Cu-37.2%Zn, the substrates were oxidized at \(450 \text{°C}\) for 4 h in 1 to 100% \(\text{O}_2\) in \(\text{N}_2\). The low magnification FESEM images of the oxidized brass wire are shown in figure 4. It is evident in low magnification image that the exfoliation of brass wire also increases with increasing the oxygen content during oxidation.

High magnification images of the Cu-37.2%Zn wire oxidized at \(450 \text{°C}\) for 4 h in 1 to 100% \(\text{O}_2\) in \(\text{N}_2\) flown at a rate of 200 sccm is shown in figure 5. Nanowires are observed on all oxidized samples. For \(\text{O}_2\) concentration of 1%, nanowires having lengths up to 2 \(\mu\text{m}\) is observed all over the oxidized surface (figure 5(a)). Increasing the concentration of \(\text{O}_2\) to 5%, the length of the nanowires is increased up to 30 \(\mu\text{m}\) (figure 5(b)). Both thin and thick nanowires are observed on Cu-37.2%Zn oxidized with 5% \(\text{O}_2\). In some instances, deposition of irregular shaped particles is seen at the top and side-walls of the nanowires. Growth of branches is observed from the irregular shaped particles, which are resolved in high magnification images (discussed in section 3.2). Further increase of \(\text{O}_2\) concentration to 10% resulted in decrease of the length of nanowires to 3–5 \(\mu\text{m}\) as seen in figure 5(c). For \(\text{O}_2\) concentration of 21%–100%, the length of nanowires decreases further and generally in the range of 1–3 \(\mu\text{m}\) as seen in figures 5(d)–(f). It is concluded that 5% of \(\text{O}_2\) in \(\text{N}_2\) flown at a rate of 200 sccm is the optimum concentration for the growth of nanowires on Cu-37.2%Zn substrate oxidized at \(450 \text{°C}\).

### 3.2. Characterization of nanowires and oxide layer

Different types of morphological variations are observed in the as-grown nanostructures on brass, such as thin morphology, thick morphology with branches, circular-flake morphology, and flat-cone morphology. Out of these, thin and thick morphology with branches are frequently observed and found in all growth conditions. However, the prevalence of thin and thick morphology with branches is more obvious for oxidizing Cu-37.2%Zn at \(450 \text{°C}\) in 1%–10% \(\text{O}_2\) in \(\text{N}_2\). One such example of thin and thick morphology with branches is shown in figures 6(a), (b) in the presence of 5% \(\text{O}_2\) in \(\text{N}_2\) flown at rate of 200 sccm at \(450 \text{°C}\). The diameter of thin nanowires is typically 50–100 nm and length is as high as 30 \(\mu\text{m}\). On the other hand, the diameter and length of the main stem of thick nanowires varies from 200–500 nm and 5–15 \(\mu\text{m}\), respectively. Generally, thick nanowires are faceted. In many instances, deposits of irregular shaped particles are observed all over the surface preferentially at the top of thick nanowires. Some branches having thin morphology are originated from the deposits creating an average angle of 60°.
with the main stem. The length of the branches varies from 1 to 3 μm.

The nanostructures resembling circular-flake morphology are randomly distributed at some localized region and sometimes mixed with thin and thick nanowires. This morphology is observed during oxidation of brass at 400 °C–450 °C in 10%–21% O₂ in N₂ flown at 200 sccm or high concentration of oxygen flown at low rate. One such example of circular-flake shaped nanostructures is shown in figure 6(c) grown at 450 °C in the presence of 100% O₂ flown at rate of 30 sccm. The circular-flake has diameter ranging from 500 nm to 1.5 μm and height is generally less than 1 μm. It

Figure 5. High magnification FESEM image of Cu-37.2%Zn wire oxidized at 450 °C for 4 h in different concentration of O₂ in N₂ having total flow rate of 200 sccm: (a) 1% O₂, (b) 5% O₂, (c) 10% O₂, (d) 21% O₂, (e) 50% O₂ and (f) 100% O₂.

Figure 6. As-grown nanostructures having different morphologies: (a), (b) thin and thick morphology with branches grown at 450 °C in the presence of 5% O₂ in N₂ flown at rate of 200 sccm, (c) circular-flake morphology grown at 450 °C in the presence of 100% O₂ flown at rate of 30 sccm and (d) flat-cone morphology grown at 600 °C in ambient.
should be noted that flake type structures were obtained by other researchers during oxidation of brass foils (Cu-34%Zn and Cu-30%Zn) at 550°C–600°C [22, 52]. The flat-cone morphology is observed during oxidation of brass wire in high concentration of O2 at 450°C or at high oxidation temperature. One such example of flat-cone morphology is shown in figure 6(d) grown in ambient at 600°C. This morphology appears to be composed of few thin nanowires where the middle one has the highest length compared with the side ones. In general, the width of flat-cone morphology is 300–600 nm at the bottom, whereas the length of the cone varies from 1 to 2 μm. The occurrence of different morphologies during oxidation of Cu-37.2%Zn wire is not clear, but it may be due to the variation of compositional non-uniformity, surface stress as well as growth conditions.

To find out the elemental compositions, EDX line scan was carried out on a few nanowires. Figure 7 shows one such EDX line scan on four (4) nanowires having thin and thick morphologies. EDX line scan across the diameter of the nanowires indicates that the counts of Zn and O are higher compared with other regions. Counts of Cu are negligible at all regions of the line scan. So, these results suggest that the nanowires are composed of Zn and O, which is ZnO. It is seen that Cu does not contribute to the formation of nanowires on Cu–Zn alloy substrates. This result is unlike of the oxidation of Ti-6%Al-4%V (wt%) substrates, where Al as alloying element contributes to the formation of nanowires [56, 58]. core–shell TiO2–Al2O3 originates on Ti-6%Al-4%V alloy substrate during oxidation [56, 58]. Such phenomenon is not observed during oxidation of brass and single ZnO nanowires are originated.

Figure 8 shows FESEM image and corresponding elemental maps of few thick nanowires composed of short branches grown on irregularly shaped deposits on the main stem of the nanowires. Presence of O and Zn is obvious in the main stem and irregularly shaped deposits (figures 8(b)–(c)), whereas the presence of Cu is uncertain (figure 8(d)). These results suggest that the composition of thick nanowires is ZnO. The compositional map of the branches is not resolved in the EDX mapping clearly but it is most likely ZnO.

Figure 9(a) shows the TEM image of ZnO nanowires with branch grown on Cu-37.2%Zn wire at 450°C for 4 h in the presence of 5% O2 in N2 flown at a rate of 200 sccm. The TEM line scan (not shown) confirms that the nanowires composed of only Zn and O, which is similar to the result obtained by FESEM line scan and elemental maps (figures 7 and 8). The presence of Cu is also not evident in the TEM line scan. This further confirms that the nanowires are composed of ZnO only. The HRTEM image focused on the main stem of the nanowires is shown in figure 9(b) and corresponding selected area diffraction (SAD) is shown in figure 9(c). The HRTEM image of the main stem shown in figure 9(b) reveals fringes having spacing of 0.28 nm, which are the regular (1 1 0) crystal plane of wurtzite ZnO. The SAD pattern shown in figure 9(c) confirms that the growth direction of the main stem is [2 1 0]. Figures 9(d) and (e) shows the HRTEM image of the branched nanowires and corresponding SAD pattern. Similar to the main stem, the branch also shows the (1 1 0) crystal plane of wurtzite ZnO having parallel alignment with the fringes of main stem as shown in figure 9(b). The growth direction of the branch is [1 1 2 0] as confirmed by SAD (figure 9(e)). It should be noted that the angle between [2 1 1 0] and [1 1 2 0] growth direction is 60°, which explains why the branches aligned at 60° angle with the main stem of the nanowires. Beside this, [2 1 1 0] and [1 1 2 0] is the same family of direction, so it can be said that the main stem and branch of the ZnO nanowires grows along (1 1 2 0) directions.

The (1 1 2 0) growth direction for ZnO nanowires grown on brass during thermal oxidation is significantly different from other ZnO nanowires grown on metallic Zn substrates. In some instances, the growth direction of ZnO nanowires on metallic Zn substrates is reported as [0 0 0 1] [44, 45]. It should be noted that the growth of ZnO nanowires on metallic Zn substrates occur at temperatures higher than the melting point of Zn (419.5°C), typically in the range of (450°C–700°C) [40–46]. So, oxidation of metallic Zn for the growth of nanowires involves liquid and/or vapor phase of Zn. Thus, the growth mechanism of ZnO nanowires on metallic Zn substrate is explained by vapor–liquid–solid (VLS) [41] or vapor–solid (VS) [43, 49] mechanism. However, in the present case, oxidation is occurred on brass substrates and no liquid phase of Zn is involved. For this reason, a different mechanism is proposed for the growth of ZnO nanowires in (1 1 2 0) direction on brass, which is discussed separately (section 3.3).

Exfoliation of the oxide is observed during thermal oxidation of Cu-37.2%Zn. One such exfoliated flake was carefully removed from Cu-37.2%Zn wire oxidized at 450°C for 4 h in the presence of 5% O2 in N2 and observed under FESEM as shown in figure 10. It is observed that oxide layer is formed and nanowires are originated on top of the oxide layer. There is no obvious direct relation of ZnO nanowires with the core brass substrate through the oxide layer. Some cracks are observed at the bottom surface of the oxide layer which may form during cooling of brass substrate.
Figure 8. (a) FESEM image of nanowires with branches grown on Cu-37.2%Zn wire by thermal oxidation at 450 °C for 4 h in the presence of 5% O₂ in N₂ and (b)–(d) corresponding EDX elemental mapping of the nanowires for O, Zn and Cu; respectively.

Figure 9. (a) Bright field TEM image of a nanowires with branch grown on Cu-37.2%Zn wire by thermal oxidation at 450 °C for 4 h in the presence of 5% O₂ in N₂, (b), (c) HRTEM image of the main stem and corresponding SAD pattern, respectively, and (d), (e) HRTEM image of the branch and corresponding SAD pattern, respectively.
To determine the chemical composition of the oxide layer beneath the ZnO nanowires, a Cu-37.2%Zn wire oxidized in 5% O₂ for 4 h at 450 °C was mounted in epoxy and polished by standard metallographic techniques. The FESEM image of the oxidized Cu-37.2%Zn wire is shown in figure 11(a). It was observed that the oxide layer is formed on top of the brass core and a gap having width of 2–20 μm has been formed between oxide layer and brass core (figure 11(a) and its inset). Figures 11(b)–(e) shows the corresponding elemental mapping of figure 11(a). It is seen that oxygen is present in the oxide layer beneath the nanowires (figure 11(b)). Zn is present both in the oxide layers and core Cu-37.2%Zn as seen in figure 11(c). However, the concentration of Zn counts is higher at the oxide layer compared with the core, which indicates the diffusion of Zn to the surface during oxidation. On the other hand, the counts of Cu are uncertain in the oxide layer, but higher in the core of the wire (figure 11(d)). This result indicates that Cu do not migrate to the surface during oxidation of Cu-37.2%Zn. So, it can be concluded that the oxide layer beneath the ZnO nanowires is composed of Zn and O, which is also ZnO. It is evident from the elemental mapping as shown in figure 11(e) that the gap and outer surface of the oxide layer is basically C, which is epoxy materials used for mounting the sample for FESEM observation. The reason for creation of such void can be explained by thermal expansion coefficient of brass and ZnO. The average thermal expansion coefficient of brass (19 × 10⁻⁶ K⁻¹) is ~6.5 times higher than the a-axis thermal expansion coefficient of ZnO (2.9 × 10⁻⁶ K⁻¹) [57]. The brass wire expands its diameter during oxidation and oxide layer forms on the surface of extended diameter. During cooling process, the brass core shrinks more than ZnO due to having higher thermal expansion coefficient resulting in a gap between the brass core and ZnO layer. This could be the reason for high rate of exfoliation of the oxide layers during high temperature oxidations as seen in figure 3.

For further confirmation of the elemental compositions, the cross-section of the oxidized Cu-37.2%Zn is line scanned and presented in figure 11(f). It is confirmed that the oxide layer is composed of ZnO, whereas the gap and the outside oxide layer is basically epoxy materials used for mounting the samples. The counts of Cu increases and Zn decreases from the core of Cu-37.2%Zn (beneath the ZnO layer) to the interface. These results clearly indicate that during oxidation only Zn migrates to the surface, suggesting diffusion based growth mechanism of ZnO nanowires.

3.3. Growth mechanism

Based on the results obtained and relevant literature survey, a mechanism is proposed for the growth of ZnO nanowires on brass substrate during thermal oxidation. The Gibbs free energies for the formation of ZnO and CuO are −320.52 KJ mol⁻¹ and −129.7 KJ mol⁻¹, respectively [59]. So, the nuclei of ZnO forms first during oxidation of brass as Cu is more nobler than Zn [51]. Even if little amount of Cu is oxidized, it will be reduced back by oxidizing Zn to ZnO by the reaction; Zn(s) + CuO(s) = ZnO(s) + Cu(s) [22, 51]. The formation of ZnO nuclei on brass is due to grain boundary diffusion of Zn atoms to the surface [60].

The Pilling–Bedworth ratio (ratio of the volumes of formed oxide and consumed metal) [61] of Zn is 1.58. This means that a protective layer of ZnO is formed during oxidation of Zn. However, in the present case brass contains only 37.2 wt% of Zn, so it is expected that the protective layer is thin. According to Cu–Zn phase diagram [54], the brass wire contains α-β phases. The α and β brasses possesses face centered cubic and body centered cubic structures, respectively. On the other hand, the formed ZnO possesses hexagonal wurtzite structures. These mismatches in volume, density and crystallographic structures between brass and formed ZnO generates compressive stress at the interface [51].

Previously, a stress induced mechanism was proposed by Kumar et al [62] to explain the growth of 1D CuO on Cu foil by thermal oxidation. The formation of simple cubic Cu₂O underneath monoclinic CuO layer during oxidation induces a substantial stress at the interface which is relaxed by forming CuO nanowires. Diffusion of oxygen form outer surface to the interface of CuO/Cu₂O layers also accumulates stress, which favors the growth of nanowires. Yuan et al [51] showed that during oxidation of brass, ZnO nanowires form on top of the existing ZnO grains instead of grain boundaries in oxide layer. It is proposed that incorporation of Zn atoms onto exiting ZnO grains is kinetically more favorable than forming new ZnO nuclei at the junctions of grain boundaries as it is not required to overcome the energy for nucleation barrier and the grain boundary diffusion channels are remained unblocked [63]. As long as the induced stress in the ZnO layer is maintained, the outward diffusion flux of Zn atoms continues and acts as a continual source of Zn cations for the growth of ZnO nanowires [63].

According to the Cu–Zn phase diagram, Cu-37.2%Zn substrate is in solid state until ~890 °C–900 °C [54]. In the present study, the oxidation temperatures are in between 350 °C and 600 °C, which is well below from the liquidus temperature of Cu-37.2%Zn alloy. The melting point of Cu,
Zn and ZnO are 1085 °C, 419.5 °C and 1975 °C, respectively. The ZnO nanowires is observed to grow below and above the melting temperature of Zn during oxidation and the highest coverage is seen at 450 °C which is above the melting point of Zn (figure 3). The ZnO nanowires grown at 450 °C contains irregular shaped particles at the top and side-walls and branches are originated from these irregular shaped particles (figure 6(b)). An oxide layer having similar composition to that of ZnO stays beneath the nanowires (figure 11). It is seen from the line scan that Zn migrates to the surface during oxidation (figure 11(f)). Based on these findings, growth mechanism of ZnO nanowires on Cu-37.2%Zn substrate is proposed during oxidation at 450 °C for 4 h in the presence of 5% O₂ in N₂. It may be noted that the proposed mechanism may differ in other growth conditions.

Under the condition of optimum oxidation temperature (450 °C), Cu and Cu-37.2%Zn alloy is in solid state. The data regarding the vapor pressure of Zn in Cu–Zn alloy is not readily available in the literature. However, the vapor pressures of pure Zn and pure Cu at 450 °C are found to be 0.491 and 3.12 × 10⁻¹⁵ mbar, respectively [64]. So, it is expected that during oxidation of brass at 450 °C, the vapor pressure of Zn is significantly higher than Cu. During oxidation, Zn segregates and diffuses toward the surface to react with oxygen for the formation of ZnO nuclei (figures 12(a), (b)). This could be regarded as the nucleation stage. Due to high vapor pressure of Zn, some of them vaporized (figure 12(b)). Over time, diffused Zn forms ZnO layer composed of small grains by reacting with oxygen (figure 12(c)). The mismatches in volume, density and crystallographic structures between formed ZnO and Cu-37.2%Zn generates compressive stress. As discussed earlier, the induced stress is released by forming new surfaces of ZnO in the forms of nanowires (figure 12(d)). The diffusion of Zn continues from the Cu-37.2%Zn core to the tip of nanowires through the side-walls [27]. It should be noted that the side-walls are facing to (0 0 0 1) planes (figure 9(d)), which may be suitable for the transportation of Zn atoms from the roots to the tips because of containing only Zn atoms in that plane [27].

The partially vaporized Zn as seen in figure 12(b), also reacts with oxygen to form ZnO and deposits on the growing ZnO nanowires (figure 12(d)). The nanowires may possess defects which may be preferable for heterogeneous nucleation of ZnO particles. The ZnO particles deposited on the family of (1 1 2 0) crystal planes, which are directed at 60° angle with the main stem of the nanowires. The deposited particles might face some sort of stress due to heterogeneous nucleation, which is relaxed by forming branches of ZnO nanowires grown at (1 1 2 0) directions (figure 12(e)). Finally during cooling, the Cu-37.2%Zn substrate shrinks more compared with ZnO layers due to having ~6.5 times higher thermal expansion coefficient (thermal expansion coefficients of brass and ZnO are 19 × 10⁻⁶ K⁻¹ and 2.9 × 10⁻⁶ K⁻¹, respectively) [57].

It should be noted that the growth mechanism of ZnO nanowires on Cu-37.2%Zn is significantly different from the nanowires grown on metallic Zn substrate. Generally, ZnO nanowires grow at temperatures in the range of 450°C–700°C on metallic Zn substrates [40–46], which is higher than the melting point of Zn (419.5°C). For this reason, the formation of ZnO nanowires on metallic Zn involves liquid and/or vapor phase and the growth mechanism is explained.

Figure 11. (a) Cross sectional view of the Cu-37.2%Zn wire after oxidation at 450 °C for 4 h in the presence of 5% O₂ in N₂ (inset showing low magnification image of cross-section), (b)–(e) corresponding elemental map of O, Zn, Cu and C, respectively and (f) line scan across the cross-section of oxidized Cu-37.2%Zn wire.
by vapor–liquid–solid (VLS) [41] or vapor–solid (VS) [43, 49] mechanism. The growth direction of ZnO nanowires on metallic Zn substrate is [0 0 0 1] [44, 45]. In the present work, no liquid or vapor phase is involved for the growth of ZnO nanowires and the stress induced mechanism is used to explain the growth of nanowires on Cu-37.2%Zn substrate. The growth direction of ZnO nanowire is \(\langle 1 1 \bar{2} 0 \rangle\) on Cu-37.2%Zn, which is different from the nanowires grown on metallic Zn. During oxidation of Cu-37.2%Zn, the Zn atoms migrate to the surface to form ZnO layer and the substrate become Cu-rich. ZnO nanowires originate from the ZnO layer by stress relaxation mechanism. It is expected that the presence of Cu-rich conductive core beneath ZnO during oxidation of brass will ease the fabrication of devices for different applications, such as opto-electronics and nano-electronics [22].

4. Conclusions

In this study, Cu-37.2%Zn substrate was thermally oxidized at different temperatures in the presence of varying concentration of \(O_2\). The following conclusions are drawn from the findings of the research work:

1. ZnO nanowires grow directly on Cu-37.2%Zn substrate by catalyst-free thermal oxidation process.
2. The highest coverage of nanowires is seen during oxidation at 450 °C in the presence of 5% \(O_2\) in \(N_2\) at a rate of 200 sccm.
3. The as-grown nanowires possess four different types of morphologies: (i) thin, (ii) thick with branches, (iii) circular-flake, and (iv) flat-cone shape structures. Out of this, the prevalence of thin and thick morphologies with branches is more prominent and seen in all growth conditions. The length and diameters of nanowires is up to 1–30 \(\mu m\) and 50–500 nm, respectively. The length of the branches varies from 1 to 3 \(\mu m\).
4. The ZnO nanowires possessed hexagonal wurtzite structure. The nanowires grow along \(\langle 1 1 \bar{2} 0 \rangle\) directions.
5. ZnO layer is formed due to Zn diffusion to the surface during oxidation of Cu-37.2%Zn substrate. The nanowires originate on top of ZnO layer.
6. Stress induced growth mechanism is proposed to explain the growth of ZnO nanowires on Cu-37.2%Zn substrate.

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