Catalyst assisted vapor phase transport growth and characterization of ZnO nanowires

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Abstract

Zinc Oxide (ZnO) nanowires (NWs) were grown on p-silicon (p-Si) substrates coated with around 10 nm thick metal films of Au, Al and Cu using vapor phase transport growth method. The effect of these metal catalysts and the substrate temperatures on the morphologies of ZnO NWs were studied using field emission scanning electron microscopy (FESEM). The growth of ZnO NWs with high aspect ratio was observed at substrate temperatures above 600 ^{o}C. The structural and optical properties of the as grown ZnO NWs were characterized using X-ray diffraction (XRD) and photoluminescence spectroscopy (PL) techniques, respectively. XRD study revealed that, the grown samples possess hexagonal wurtzite structure with (002) preferential orientation. The metal droplets were observed at the tips of ZnO NWs when Au was used as catalyst, but not in the case of Al and Cu. The PL spectra exhibited two peaks, one in the UV region and the other in the visible region. The low-cost Al and Cu metal catalyst assisted growth of metal contamination-free ZnO NWs may be suitable for the device applications.

Keywords: ZnO, nanowires, metal catalyst, two zone furnace, vapor phase transport growth.

Introduction

The nanosize material structures have attracted great interest because of their unique physical and chemical properties. Various kinds of nanostructures such as nanorods, nanowires, nanobelts, nanotubes, nanowalls, nanohelixes, and nanorings of various semiconductor materials have been synthesized **[1]**. Among them, the one-dimensional nanostructures such as nanowires have attracted great attention for their potential applications in nanoscale electronic and optoelectronic devices **[2]**. Among various semiconductor materials, ZnO NWs are considered as the most promising one because of their band gaps coinciding with the UV region of the electromagnetic spectrum and also ZnO possesses large exciton energy (60 meV) that could lead to lasing action based on exciton recombination at room temperature **[3]**.

ZnO NWs have been synthesized by different growth techniques such as vapor phase transport growth method (VPT), RF magnetron sputtering, molecular beam epitaxy (MBE), pulsed laser deposition (PLD), laser-assisted catalytic growth, solution phase methods, chemical vapor deposition (CVD), and metal organic chemical vapor deposition (MOCVD) **[4]**. Among the different growth methods, vapor phase transport growth method is a simple and low-cost technique used for the growth of high quality ZnO NWs **[5]**. The growth of ZnO NWs is proposed to takes place under any one of the following mechanisms: (1) vapor-liquid-solid (VLS), (2) vapor-solid (VS) process, and (3) vapor-solid-solid (VSS) process **[6]**. In VLS process, a metal liquid droplet serves as a preferential site for absorbing the vapor reactant. NW growth begins when the droplet is supersaturated with the source material, and growth continues as long as the droplet remains in the liquid state and vapor is supplied. The appearance of the metal droplets on the tips of the NWs is considered as the characteristic feature of VLS growth process **[7]**. The VS mechanism is generally used to describe catalyst-free growth of ZnO NWs. The VS mechanism results in the growth of nanostructures with variety of morphologies **[8]**. In VSS mechanism, the metal catalyst in the solid state acts as preferential site to initiate and guide the growth of one dimensional NWs **[9]**. The ZnO NW growth using vapor phase transport process is achieved by coating a thin film of metal catalysts such as Au, Sn, Al, Ag, Pt, Pd, Cu, Ni and Fe on the substrates **[10]**. Au is found to be most commonly used catalyst in the growth of ZnO NWs, but the cost effectiveness of Al and Cu compared to Au also

makes them efficient catalysts. It is interesting to investigate the growth related aspects using different catalysts and there are several reports on the ZnO NWs using different catalysts. Zhang et al. investigated the effects of Au, Pt, and Ag catalysts assisted ZnO NWs growth. The selection of metal catalyst is important for the growth of the desired NWs without any contamination **[11]**. Badran et al. synthesized ZnO nanorods on Si substrate by thermal evaporation for the fabrication of p-Si/n-ZnO heterojunction diode **[12]**. Wen et al. studied the structure, growth kinetics, and ledge flow during VSS assisted vapor phase transport growth of copper catalyzed silicon NWs **[13]**. Wongchoosuk et al. presented a systematic study on the growth of ZnO nanostructures in a thermal CVD system focusing on the source temperature and substrate temperature by keeping all other parameters constant **[14]**. Mohanta et al. investigated the effect of pressure and Al doping on structural and optical properties of ZnO NWs synthesized by chemical vapor deposition **[15]**. Zandalazini et al. studied the growth of Al catalyst assisted ZnO nanostructure by vapor phase transport technique and they concluded that VSS mechanism is responsible for the growth of ZnO nanostructures instead of VLS or VS mechanism **[6]**. Chhikara et al. studied the growth and field emission properties of vertically-aligned ZnO NW array on biaxially textured Ni-W substrate by thermal evaporation **[16]**.

In this paper, we report the growth of ZnO NWs on Si substrates coated with thin film of Au, Al, and Cu metal catalysts using vapor phase transport method at different substrate temperatures. The grown ZnO NWs were investigated for the structural, morphological and optical properties using XRD, FESEM and room temperature PL measurements, respectively. The main objective of the present work is to grow high quality ZnO NWs suitable for device applications using a simple low-cost vapor phase transport growth system.

Experimental

Materials

ZnO powder (Sigma Aldrich, 99.999 %) and graphite powder (Sigma Aldrich, 99.99 %) in the weight ratio of 1:1 is used as a source material. p-Si (100) is used as a substrate and Au, Al and Cu metal films were used as catalysts. Argon (99.9996 %) and oxygen gases (99.83 %) were used as carrier gas and reactive gas.

Methods

ZnO NWs were grown on p-Si substrates by Au, Al, and Cu metal catalyst assisted vapor phase transport growth method. A home-made two-zone horizontal furnace based vapor phase transport growth system was used for the growth of ZnO NWs. The schematic diagram of the growth system is shown in **Fig. 1**. The growth system consists of a two-zone horizontal furnace of length 60 cm with both end open and a quartz tube of 100 cm in length and 32 mm in diameter fitted with stainless tube quick coupling to facilitate sample loading, evacuation, source and gas flow. Shimaden Co. Ltd. Japan SR1 PID temperature controllers were used to control the temperature of the two-zone furnace. The gas flow rates were monitored using Alicat Scientific, Inc. (USA) made MC-500SCCM-D mass flow controllers. The p-Si substrates, used for growth were cleaned using organic solvents, dipped in HF acid to remove native SiO_2, washed with double distilled water and dried under nitrogen blow. The thin films of Au, Al and Cu of about 10 nm in thickness were deposited on p-Si substrates by thermal evaporation (HINDHIVAC vacuum coating unit- Model 12A4). For ZnO NWs growth, the source powders of ZnO and graphite were mixed at a weight ratio of 1:1 and loaded in a small quartz boat and placed inside the quartz tube at the centre of zone of the furnance. The substrates were placed at the centre of Zone 2 of the furnace. After loading the source material and substrates, the quartz tube was evacuated using rotary vacuum pump to a vacuum level of about 0.02 mbar. The growth of ZnO NWs were carried out by maintaining the source temperature at 1000 ^oC and the substrates temperatures at 500 ^oC, 600 ^oC, 700 ^oC, and 800 ^oC. Argon flow rate was maintained at 150 sccm. When the temperature of the source reaches 900 ^oC, oxygen gas was introduced at flow rate of 15 sccm. The growth was carried out for one hour. The change in the color of the substrates after the growth indicates the deposition of the film. The structural, morphological and optical properties of the grown ZnO NWs were investigated.

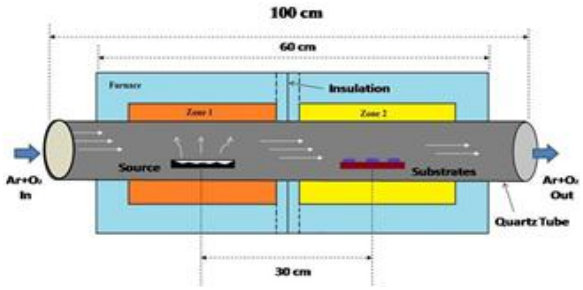

Fig. 1. Schematic diagram of the vapor phase transport growth system having two-zone furnace.

The XRD patterns of the grown samples were studied using the Rigaku Miniflex–600 X-ray diffractometer with a scan rate of 1 degree per minute and 2θ varying from 30^o to 80^0. XRD was operated at a voltage of 40 kV and a current of 15 mA using CuKα radiation of 0.514 nm. The surface morphologies of the grown samples were studied Ultra 55 Carl-Zeiss FESEM. The PL spectrum was recorded using Acton Spectra Pro 2500i monochromater equipped with He – Cd laser in the wavelength range of 350 – 800 nm and with an excitation wavelength of 325 nm.

Results and discussion

Fig. 2(a) – 2(c), shows the XRD patterns of ZnO NWs grown at 700 ^{o}C on Au, Cu and Al coated Si substrates, respectively. The observed XRD patterns were found to match with the hexagonal wurtzite structure of ZnO (JCPDS data card number 36–1451). The XRD spectra of ZnO NWs dominated by (002) direction, indicates the preferred growth direction is along c – axis.

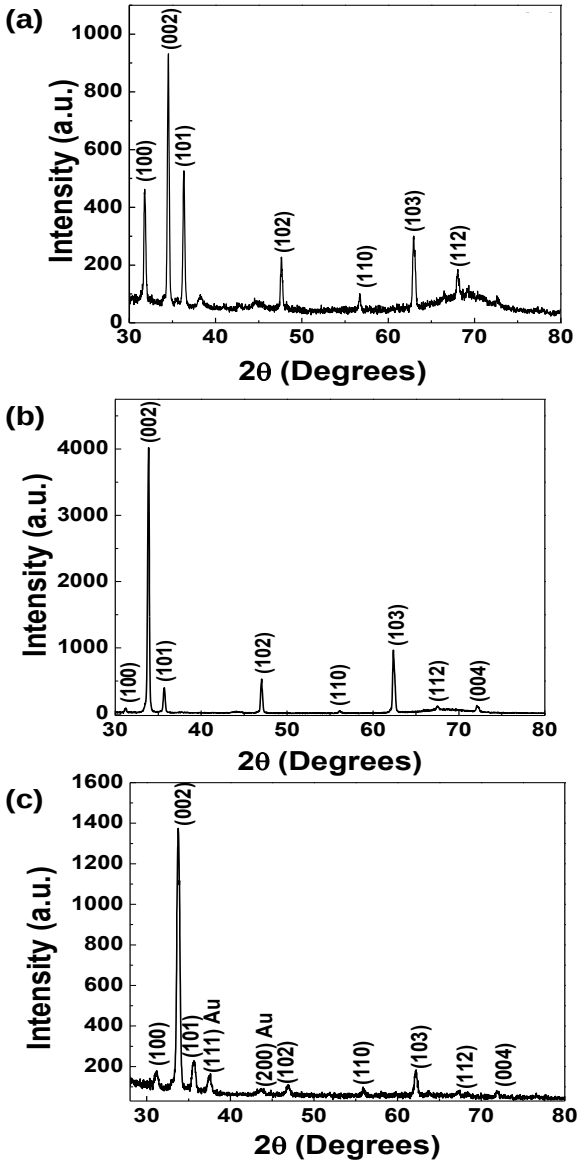

Fig. 2. XRD patterns of ZnO NWs grown on (a) Au, (b) Al and (c) Cu coated Si substrates.

Fig. 3(a) – 3(d) shows the FESEM images of ZnO NWs grown on Au coated Si substrates at temperature of 500 ^{o}C, 600 ^{o}C, 700 ^{o}C, and 800 ^{o}C, respectively. At 500 ^{o}C, the formation of nano-particles were observed as shown in **Fig. 3(a).** As the temperature was increased to 600 ^{0}C, the formation of dense and uniformly distributed NWs were observed. It is observed that thickness of the NWs have been increased with increasing the substrate temperature to 800 ^{0}C.

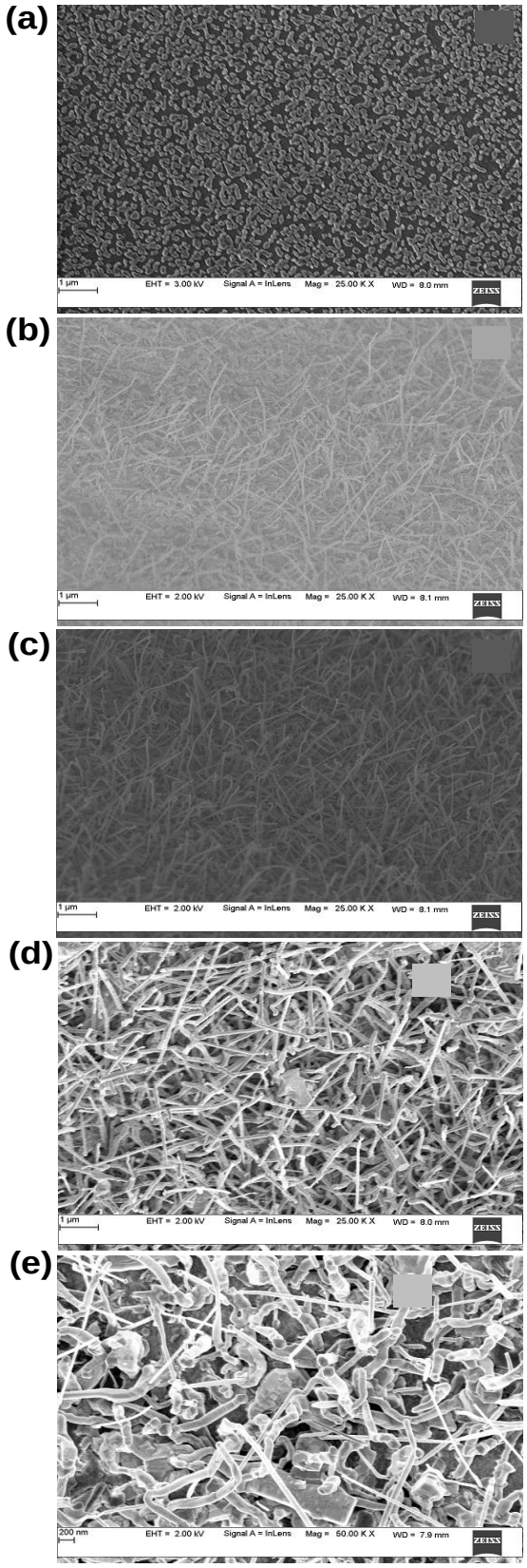

Fig. 3. FESEM images of ZnO NWs grown on Au coated Si substrates at temperatures (a) 500 ^{o}C, (b) 600 ^{o}C, (c) 700 ^{o}C and (d) 800 ^{o}C, and (e) magnified image of the ZnO NWs grown at 800 ^{o}C showing Au droplets at the tip.

Fig. 3(e) shows the magnified FESEM image of the ZnO NWs grown on Au coated Si substrate at 800 ^{o}C with Au droplets at the tip of the NWs. The formation of ZnO NWs on Au coated Si substrates can be explained as follows. When the Au coated Si substrate is heated above the melting point of Au–Si (363 ^{o}C), a large amount of Au droplets will be formed on the surface of Si substrates. These nanoscale liquid droplets absorb Zn and oxygen vapors to form ZnO and over time supersaturates in the droplets. At supersaturation, ZnO precipitates at the solid-liquid interface to form ZnO, leaving Au droplets at their tip. The repeated process of absorption of Zn and oxygen vapors into Au droplets and precipitation of ZnO solid-liquid interface at superstation leads to the formation of ZnO NWs **[17]**.

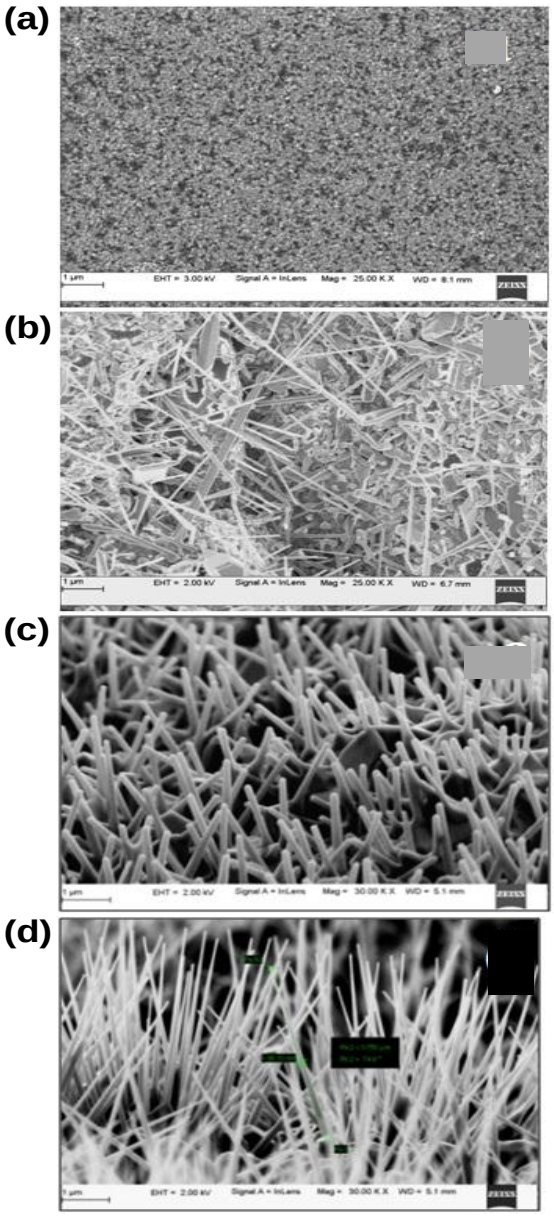

Fig. 4. FESEM images of ZnO NWs grown on Al coated Si substrates at temperatures (a) 500 ^{o}C, (b) 600 ^{o}C, (c) 700 ^{o}C, and (d) 800 ^{o}C.

Fig. 4 (a) - **4 (d)** shows FESEM images of ZnO NWs grown on Al coated Si substrates at temperature of 500 ^{o}C, 600 ^{o}C, 700 ^{o}C, and 800 ^{o}C, respectively. **Fig. 5 (a)** - **5 (d)** shows FESEM images of ZnO NWs grown on Cu coated Si substrates at temperature of 500 ^{o}C, 600 ^{o}C, 700 ^{o}C, and 800 ^{o}C, respectively. In the the FESEM images of ZnO NWs grown on Al and Cu coated Si substrates, we do not observe any metal droplets at the tips of the NWs.

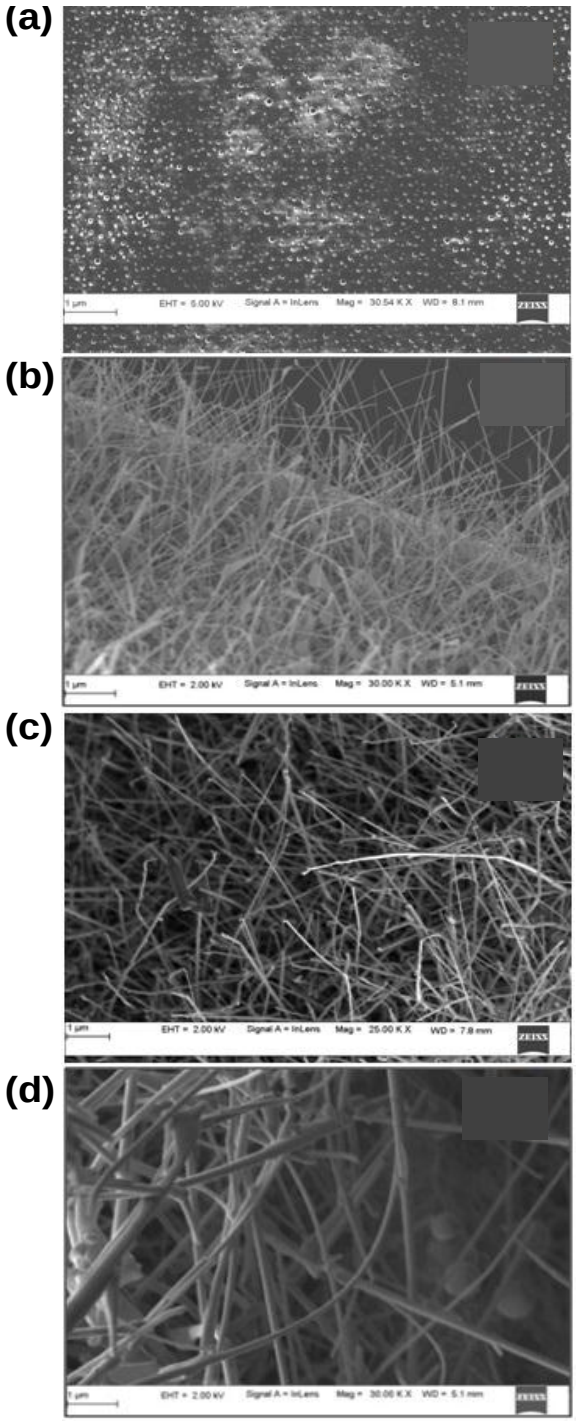

Fig. 5. FESEM images of ZnO NWs grown on Cu coated Si substrates at temperatures (a) 500 ^{o}C, (b) 600 ^{o}C, (c) 700 ^{o}C and (d) 800 ^{o}C.

In this case, the growth of ZnO NWs may be taking place via VSS mechanism. This may be due to the non-formation of Al and Cu metal liquid droplets at the substrate temperature used in this work or may be due to the oxidation of Al and Cu thin films during the ZnO NWs growth process. Therefore, the Al and Cu films in solid form or in oxidized from act as preferential sites for the initiation of ZnO NWs growth via VSS mechanism [**6, 13**].

Room temperature PL spectra of ZnO NWs deposited on Au, Al and Cu coated Si substrates at 700 ^{o}C by vapor phase transport growth method is shown in **Fig. 6(a) – 6(c),** respectively. The PL spectra shows a sharp near band edge emission (NBE) peak in the UV region and a broad deep level emission (DLE) peak in the visible region. In the PL spectra, NBE peaks at 383 nm, 385 nm and 384 nm attributed to exciton transition and DLE peaks at 511 nm, 570 nm and 503 nm is usually attributed to the oxygen states related to lattice defects **[18]**.

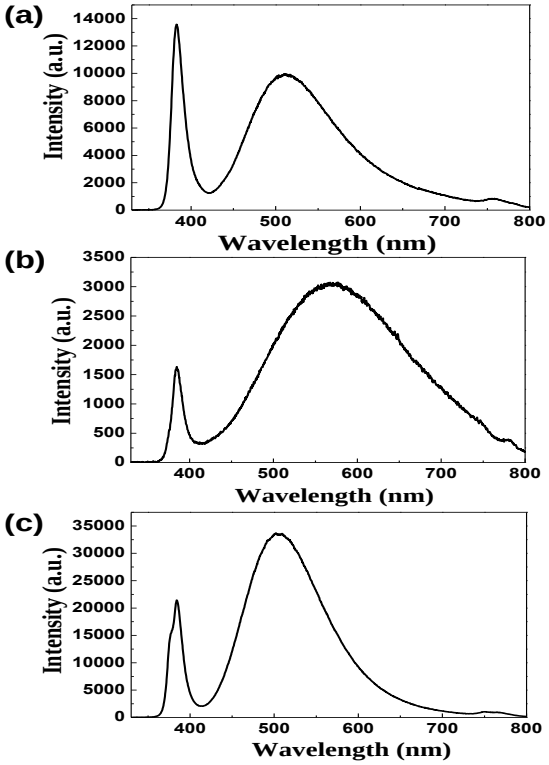

Fig. 6. PL spectra of ZnO NWs grown on (a) Au, (b) Al and (c) Cu coated Si substrates.

Conclusion

The ZnO NWs were successfully grown on different metal catalyst coated p-Si substrates by vapor phase transport growth method. The structural, morphological and optical properties of the grown ZnO NWs were characterized by XRD, FESEM and PL techniques, respectively. The effect of different metal catalyst used and the substrates temperature on the morphology of the as grown ZnO NWs were studied using FESEM. The optical properties of the as grown NWs were studied using room temperature PL spectroscopy. The metal catalysts were observed on the tips of ZnO NWs using Au catalyst, where as no metal catalysts tips were observed in Al and Cu metal catalysts assisted growth. Hence Au catalyst assisted growth of ZnO NWs takes place through VLS mechanism and in the case of Al and Cu, growth occurs due to VSS mechanism. The low-cost Al and Cu metal catalyst assisted ZnO NWs may find application for the metal contamination-free ZnO NWs devices. Our results indicate that along with Au, both Al and Cu works as excellent catalysts for the production of ZnO NWs and thus find potential applications in many fields.

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