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Synthesis of Cu_2O and ZnO Nanowires and their Heterojunction Nanowires by Thermal Evaporation: A Short Review

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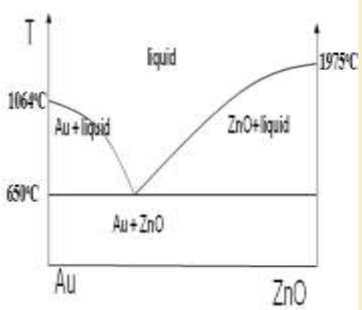
Graphical abstract



Abstract

One dimensional metal oxide semiconductor nanowires of copper (I) oxide (Cu_2O), zinc oxide (ZnO), and their heterojunction nanowires possess remarkable physical and chemical properties. ZnO and Cu_2O areattractive because the metals are abundant on earth, inexpensive, nontoxic.Moreover, these oxides have useful optical and electrical properties suitable for a wide variety of electrical devices, because their electrical conduction can be predictably controlled by doping. We here restrict the disscussion using a Hot Tube Vacuum Thermal Evaporation. The NWs in these devices will be studied by physical vapor deposition known as vapor-liquid-solid (VLS). Therefore, we explore conventional methods, particularly the VLS of growing ZnO and Cu_2O nanowires which are assisted by the catalyst. In this short review, we report the individual and combined (Cu_2O/ZnO) junction nanowires by PVD method. The main advantages of these composite nanowires are the natural p-n characteristics, the broad light absorption, the high sensitivity to humidity changes, and the fast dynamic response. The combination of all characteristics offered by Cu_2O/ZnO nanowires can enable the fabrication of diverse sensing devices, and photovoltaic solar cells.

Keywords: Thermal evaporation, Heterojunction, Cu_2O Nanowires, ZnO Nanowires.

Abstrak

Dawai nano logam oksida semikonduktor satu dimensi seperti kuprum (I) oksida, Zink Oksida (ZnO), dan dawai nano heterojunction lain memiliki sifat-sifat fizikal dan kimia yang luar biasa. ZnO dan Cu_2O mempamerkan ciri-ciri menarik kerana mereka tergolong sebagai logam yang senang didapati di muka bumi selain berharga murah dan tidak beracun. Selain itu, oksida ini juga mempunyai ciri-ciri optik dan elektrik yang sesuai digunakan untuk pelbagai jenis alat-alat elektrik kerana pengaliran elektrik mereka boleh diramal dan sekaligus dikawal oleh kaedah pendopan. Perbincangan ini dihadkan kepada penggunaan kaedah penyejatan Hot Tiub Termal Vacuum. Dawai logam ini dikaji berdasarkan teori pemendapan wap fizikal yang dinamakan teori wap-cecair-pepejal (VLS). Kaedah VLS merupakan kaedah konvensional yang biasa digunakan terutama di dalam proses pertumbuhan dawai logam ZnO dan Cu_2O yang melibatkan penggunaan pemangkin. Dalam kajian pendek ini kami melaporkan kedua-dua jenis dawai nano logam iaitu individu dan gabungan dawai nano persimpangan (Cu_2O / ZnO) melalui kaedah PVD. Kelebihan utama dawai nano yang dihasilkan melalui kaedah ini ialah mereka mempunyai sifat-sifat semula jadi pn, sebagai penyerap cahaya yang bagus, kepekaan yan tinggi terhadap perubahan kelembapan sekeliling serta tindak balas dinamik yang pantas. Gabungan ciri-ciri hebat oleh dawai nano Cu_2O / ZnO ini dapatmembantu dalam penghasilan peranti pengesan pelbagai dan sel-sel solar photovoltaic secara lebih meluas.

Kata kunci: Penyejatan termal, heterojunction, dawai nano Cu2O, dawai nano ZnO

■1.0 INTRODUCTION

In recent years the research on one-dimensional (1-D) nanostructures of different materials have been attracted much attention and their use for devices have been increasing. The reason for this is the unique and exceptional properties of nanostructures, which are different from bulk materials. This is due to the dependence of the chemical and physical properties of nanostructures on size. One-dimensional nanostructures, including nanowires (NWs) and nanorods are the most studied nanomaterials for their important physical properties and application prospects. High aspect ratio, extremely large surface-to-volume ratio, high porosity and direct carrier conduction path of 1D nanostrucres are the key factors for getting edge over other type of nanostructures. These properties would lead to potential use for realizing advanced nanoscale applications in photovoltaics, nanogenerators, field emission devices, sensing, efficient energy conversión and storage devices.[1-3]

The field of semiconductor nanowire has become one of the most active research area within the nanoscience and technology.[4-5] Many materials are under focus with the potential of developing nano-systems.The optimization of the performance is the main challenge at the moment. The materials to be discussed are copper (I) oxide (Cu_2O), zinc oxide (ZnO), and their heterojunction. To grow these nanowires both high temperature methods and low temperaturas methods are being extensively used. In this paper, we restrict to high temperatura methods of hot tube vacuum thermal evaporation method.

Copper (I) oxide (Cu_2O) is an attractive material with semiconducting property. It has a stable and intrinsic p-type semiconductors with direct band gap energy 2.1 eV and high absorption coefficient. Their band gaps make them good candidates for photovoltaic devices (e.g. solar cells and devices which use photolysis of water to obtain hydrogen), catalysts, sensors (for gas or liquids[6,7]), stable electron sources and optoelectronic devices.[8-10] Copper oxide NWs are particularly desirable due to their large surface areas. Larger surface areas lead to higher absorption of photons in photovoltaic devices which results in greater efficiency.[11,12] Similarly, in sensors large surface areas mean a higher probability of species adsorption which leads to a better response.[13,14] For an electron source, a larger electric field at the tip of the NW can be achieved with the same applied potential as in classical field emission sources. In addition, the surface to volume ratio of a NW is considerable which means that surface processes largely prevail over the processes in the bulk material. This is evident as the properties of the NWs are different from the properties of the bulk material. It has already been reported that a shift in band gap was observed in copper oxide NWs and nanocrystals.[15,16] In addition Cu_2O nanowires (NWs) can be potentially applicable in gas sensing, magnetic storage media, in nano-devices for catalysis and for field emitter devices.[17]

While Zinc Oxide (ZnO) is another metal oxide semiconductor is quite popular due to easiness of growing it in the nanostructure form. The direct wide band gap of ZnO ~ 3.4eV is suitable for short wavelength optoelectronic applications, while the high exciton binding energy ~ 60meV allows efficient excitonic emission at room temperature.[18] Moreover ZnO, in addition to the ultraviolet (UV) emission, emits covering the whole visible region i.e. containing green, yellow and red emission peaks.[19-21] The emission in the visible region is associated with deep level defects. Generally oxygen vacancies (Vo), zinc vacancies (VZn), zinc interstitials (Zni), and the incorporation of hydroxyl (OH) groups in the crystal lattice during the growth of ZnO are most common sources of the defects related emission.[22,23] ZnO naturally exhibits n-type semiconductor polarity due to native defects such as oxygen vacancies and zinc interstitials. P-type doping of ZnO is still a challenging problem that is hindering the possibility of a p-n homojunction ZnO devices. Furthermore, the remarkable properties of ZnO like being bio-safe, bio-compatible, having high-electron transfer rates and enhanced analytical performance are suitable for intra/extra-cellular sensing applications.[24-26]

Alternatively using heterojunction nanowires approach, researchers are able to modify/improve the selective property of the oxide nanowires. Oxide nanowires are expected to have improved charge collection efficiency because of the lower interval and higher contact area between the p-type and n-type materials. Recently, some studies on Cu_2O/ZnO nanowire heterojunction solar cells have been reported. However, in the case of Cu_2O deposited by the sputtering method on the ZnO nanowires, the Cu_2O layer did not fill the spaces between the nanowires.[27]

In this short review article, first we present a summary of the widely used technique for the growth of high quality Cu_2O and ZnO NWs and fabrication methodologies for Cu_2O/ZnO heterojunction nanowire. We present some of our recent results on the growth and synthesis of Cu_2O and ZnO NWs by hot tube vacuum thermal evaporation method.

■2.0 GROWTH TECHNIQUES

The growth of Cu2O and ZnO and their heterojunction through many techniques has been discussed widely along with the applications. Our work is based grown by vapor transport as well as by Hot Tube Vacuum Thermal Evaporation method.

2.1 Vapor Transport Method

Recent progress in the synthesis and characterization of nanowires has been driven by the need to understand the novel physical properties of one-dimensional nanoscale materials, and their potential application in constructing nanoscale electronic and optoelectronic device.24 Nanowires with different compositions have been explored using various methods including the vapor-phase transport process, chemical vapor deposition, arc discharge, laser ablation, solution, and a template-based method.23-26 Chemical vapour deposition is the most prominent method of deposition nanowires. According to the difference on nanostructure formation mechanisms, the extensively used vapor transport process can be categorized into the catalyst free vapor-solid (VS) process and catalyst assisted vapor-liquid-solid (VLS) process.

2.1.1 Vapor-Liquid-Solid (VLS); Catalyst Assisted

VLS technique was first introduced to the world by Wagner and Ellis28 in 1964. They used Au particles as catalysts to grow crystalline semiconductor whiskers from vapor sources such as SiCl4 and SiH4. The Au particles deposited on the surface of a Si substrate react first with Si to form Au-Si alloy droplets at a certain temperature. It is observed that, the melting temperature of the Au-Si alloy at the eutectic point is very low which is about 363°C compared with the pure Au or Si. They both can form solid solution for all Si content.at a temperature above 363°C, Au particles can form Si-Au eutectic droplets on Si surfaces and the reduction of Si occurs at Au-Si droplets due to a catalytic effect. The Au-Si droplets absorb Si from the vapor phase resulting in a supersaturated state. Since the melting point of Si is 1414°C that is much higher than that of the eutectic alloy, Si atoms form a precipitate from the supersaturated droplets and bond the liquid-solid interface, and the liquid droplet rises from the Si substrate surface. The typical feature VLS mechanism is its low activation energy compared with normal vapor-solid growth. The whiskers grow dominantly in the areas which full of nucleation sites produced by the metal catalysts and their diameters are determined by the sizes of the catalysts.

Besides the formation of Au-Si alloy, it is believed that there is a formation of Au-ZnO alloy as well. The nucleation of gold will form nucleation site on the Si substrate. Eutectic condition is achieved at ~650°C as shown in curve of Figure 2.1 where the melting point of the alloy becomes lower. As more ZnO vapors coming Au nucleus, it will start to form precipitation at temperature approximately at 960°C to allow it to diffuse into nucleation site. As crystallization process continued, whiskers are formed vertically and ZnO nanowires eventually formed. If the growth is allowed to continue, the nucleus of Au probably will gradually disappearing and leaving the whiskers behind.

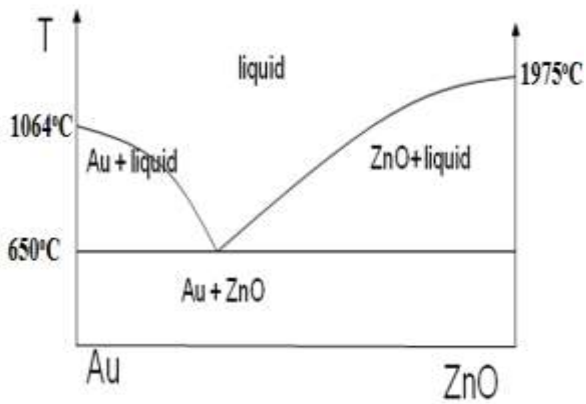


Figure 2.1 Au-ZnO phase diagram and its eutectic point

As reported by Y. Sonia[29], the nanowires are grown via the VLS mechanism using gold as catalyst. Zinc oxide powder and graphite powder with ratio of 1:1 were place in an alumina crucible inside the furnace. The silicon samples with orientation of (100) were placed with 20 nm gold patterns on them facing downstream from the crucible. As the temperature of the crucible increased to ~ 1000°C, the ZnO powder was reduced by graphite to form zinc and CO vapors. The corresponding chemical reaction can be expressed as [30, 31]:

$$ZnO(s) + C(s) \rightarrow Zn(g) + CO(g) \qquad (2.1)$$

$$CO(g) + ZnO(s) \rightarrow CO2(g) + Zn(g) \qquad (2.2)$$

The argon gas carried the zinc, CO and CO_2 vapors to the samples. Meanwhile the formation of eutectic alloy droplet occurred at each catalyst site. The gaseous products produced by the above reactions would adsorb and condense on the alloy droplets. Subsequently, the following reaction was catalyzed by the Au-Si alloy at solid-liquid interface to obtain zinc oxide nanowires.[30, 31]

$$Zn(g) + CO(g) \rightarrow ZnO(nanowire) + C(s) \qquad (2.3)$$

$$C(g) + CO_2(g) \rightarrow 2CO(g) \qquad (2.4)$$

The zinc vapor saturated the alloy droplet, followed by the nucleation and growth of solid ZnO nanowire due to the super saturation of the liquid droplet. Further growth of the nanowire taking place at the droplet interface constantly pushes the catalyst upwards. Thus, such a growth method successfully provides site-specific nucleation at each catalytic site.The VLS crystal growth method is undoubtedly the most widely adopted approach to grow semiconductor nanowires because of its great flexibility. VLS nanowire growth involves three distinct stages: alloying, nucleation, and growth.[32]

2.1.2 Vapor-Solid (VS); Catalyst Free

Without the aid of a catalyst, the Vapor-Solid (VS) growth has become the most frequent technique used to synthesize metal oxide and some semiconductor material.

Kouklin[33] has studied about doped ZnO nanowires and its application in multispectral photodetection. It is observed that ZnO and SnO_2 were reduced by powdered carbon at high temperature. As a result, Zn and Sn vapors were released simultaneously. The vapors that produced then transferred and diffused onto the substrate and directly reacted with the existing oxygen in the quartz tube to form doped ZnO seeds. In order to maintain the growth of Sn doped ZnO nanowires, the gas phase has to continuously supply the atoms for the seeds absorption process on the substrate.

By Shou-Yi *et al*.[34] vertically aligned ZnO nanowire (NW) arrays have been synthesized on silicon substrates by chemical vapor deposition. The growth of ZnO NWs may be dominated by vapor-solid nucleation mechanism

In another study, Kong *et al*.[35] successfully synthesized complex ZnO nanostructures such as nanobelts and nanohelixes. Zn^{2+} and O^{2-} ions were decomposed from ZnO powder at nearly 1350°C with the presence of Ar carrier gas. Alumina is used as the substrate and it is where the nanostructure deposition occurs at low temperature of 400 to 500°C in this process, nanostructures are produced by condensing directly from vapor phase. However, VS process has its own disadvantage on how it is difficult to control the geometry, alignment and precise location of ZnO nanostructures.

2.2 Hot Tube VaccumThermal Evaporation Method

Hot Tube VaccumThermal evaporation of solid source material is a simple method to fabricate nanowires and other interesting nanostructures. The experimental setup does not require huge number of instrument and material as shown in Figure 2.2. There are two critical parameters which is temperature gradient and the vacuum conditions that need to be controlled well for the formation of nanowires to be succeeded. Metal oxides like ZnO, SnO_2, In_2O_3, CuO Cu_2O etc are very suitable for this type of fabrication technique. The fabrication of these nanowires is simply through evaporating commercial metal oxide powders at elevated temperatures under a vacuum or in an inert gas atmosphere with a negative pressure. Nanowires form at low temperature region where materials deposit from the vapor phase. The process where the nanowires are generated directly from the vapor phase in the absence of a metal catalyst is called Vapor-Solid (VS) process.[34] Vacuum conditions are sometimes needed in order to generate the vapor phases of the source materials because some materials may not sublimate in the normal atmosphere.[36] However, there is another effective way to generate the vapor source materials in a normal atmosphere. Additional material could be added and allowed to react with the source material. By adding carbon powder to react with the ZnO source, Zn or Zn-suboxide vapor phases can be easily generated at 1000°C and the most interesting part is this process does not require any carrier gases and catalyst. However, the temperature is critical for the formation of different forms of ZnO nanostructures.

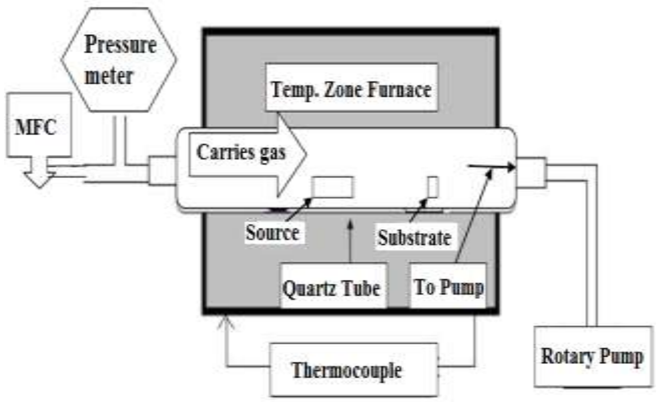


Figure2.2 A simple experimental setup of the thermal evaporation

3.0 SYNTHESIS OF CU_2O NANOWIRES BY HOT TUBE VACCUMTHERMAL EVAPORATION METHOD

Cu_2O nanowires were grown on the Cu substrates by thermal oxidation in oxygen rich environment using thermal evaporation system of vacuum quartz tube furnace .The growth parameter of Cu_2O Nanowires is shown in table 3.1

At first the samples were oxidized at 400 ◦C for time 1h and then at 400 ^{0}C for 1/2 h for studying the effect of the time and temperature on the morphology as shown in figure 3.1 and figure 3.2. It can be seen from figure 3.1(a,b) and figure 3.2(a,b) the morphologies of oxide scales formed at 400 ^{0}C, showing high density of uniformly curved nanowires, with diameter in the range of 25-100nm and length of 1-3 um. In the figure 3.1(a,b) that the nanowires with short length of 2.10 micro meter and the diameter is found in the range of 84.2 nm is shown.

Table 3.1 Growth parameters of Cu_2O Nanowires

S.N0.	Substrate	Thickness	Oxidation temperature	Oxidation temperature	Flow rate of Oxygen(mass flow meter)	Elemental weight% of Cu :O (EDX)
1	Cu foil (S1)	0.5mm	400	1hour	0.09psi	30.46:5.54
2	Cu foil (S4)	0.5mm	400	1/2hour	0.12psi	26.59:8.82

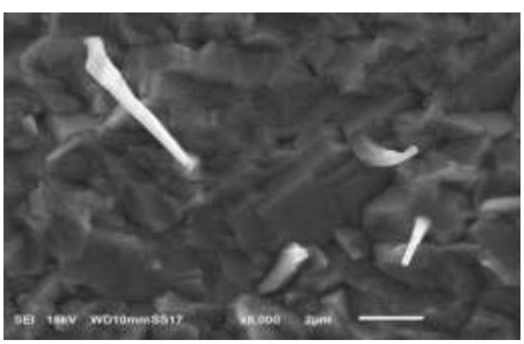


Figure 3.1(a) FESEM images of Cu_2O nanowires(S1)

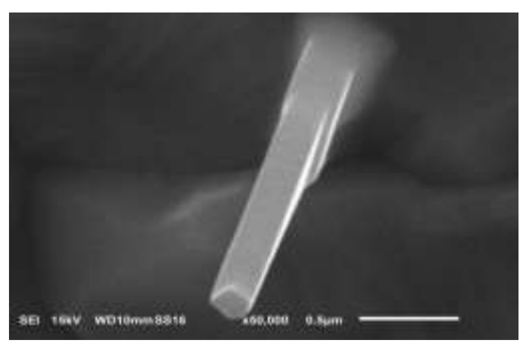


Figure 3.1(b) FESEM images of Cu_2O nanowires(S1)

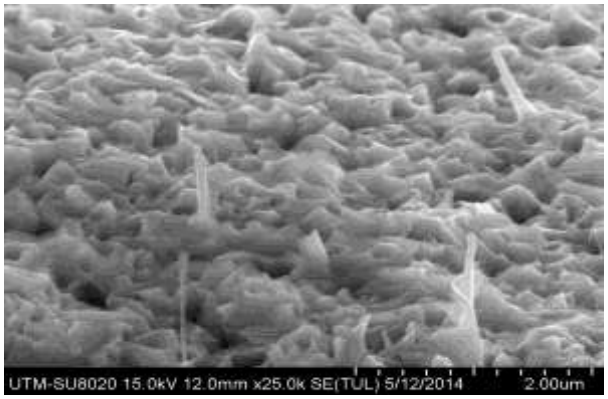


Figure 3.2(a) FESEM of tilt images of Cu_2O nanowires grown on the Cu foils by thermal oxidation in rich oxygen by vacuum furnace of quartz tube of thermal evaporation (S4)

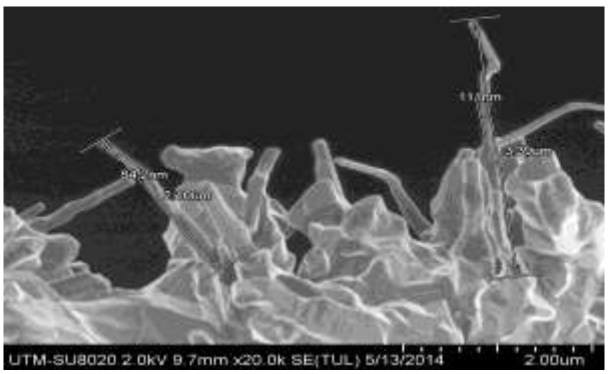


Figure 3.2(b) FESEM of tilt images of Cu_2O nanowires grown on the Cu foils by thermal oxidation in rich oxygen by vacuum furnace of quartz tube of thermal evaporation (S4)

■4.0 FUTURE WORKS

The next stage for this experiment will be the doping processes with individual metal oxides and synthesis their pn junction of Cu_2O/ZnO NWs. System's modification will be made. Doped metal oxide nanowires will be grown by the metal-catalyst growth mechanisms. New interesting result will be obtained from photoluminescence, field emission and magnetic properties due to the introduction of doping of each metal oxide and the combine heterojunction of Cu_2O/ZnO NWs . Doping will alter the conductivity levels of semiconductors, thus enhancing electrical properties. In this study, we investigate the optimal VLS deposition condition of Cu_2O absorber layers by controlling the deposition times, substrate temperatures and flow rates. The electrical, structural, morphological, and optical properties of the Cu_2O layers for different experimental conditions will be studied in details using the specific measurements (FESEM, HRTEM, PL, XRD, etc.). Also, the ZnO nanowire arrays will be grown by a thermal evaporation with horizontal quartz glass tube to enhance the charge collection and reduce the defect states at the Cu_2O/ZnO interface.

Doped metal oxides and Cu_2O/ZnO NWs nanowire is potentially used in many applications, such as photocatalytic performance and sensing device. Besides that, the measurement of electrical properties doped metal oxides and Cu_2O/ZnO NWs nanowires will also carried out with the aid of four-point probe equipment and later, the application of these nanostructures is investigated based on selected sensors technology such as gaseous sensors, liquid sensors and photovoltaic application.

■5.0 CONCLUSION

The outcome of this research is to produce Cu_2O, ZnO and their heterojunction NWs by using evaporation technique. This technique is practical to be used because it can provide stability and maintain the formation of the nanostructures grown. The thickness and size of the nanowires can be controlled by means of several actions for example varying the temperatures reading during the experiment and so on. This method is also found to be the simplest, cheapest and most effective way to synthesis Cu_2O, ZnO and their heterojunction (Cu_2O/ZnO) NWs. The understanding of nucleation and growth mechanism will give impetus to a better research finding within the scope of nanowires and their use for sensing and photovoltaic applications.

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