# CHAPTER 1

# Introduction

## 1.1 Principles, Theory, Rationale and/or Hypotheses

Nanomaterials are currently attracting much interest due to their properties for applications in nanoscience and nanotechnology. The properties of nanomaterials are dependent on their morphology. Two major effects of nanostructure material are the size dependent effect and the high surface-to-volume ratio. Firstly due to size dependent effect, the properties of nanostructures are different from the properties of microstructures or bulk. For example, density of state (DOS) at different size dependent the different functions are shown in Figure 1.1. For 3 dimensions, DOS is a continuous function with respect to energy and is related to the square root of energy. For 2, 1 and 0 size dependent, the DOSs are discrete functions with respect to energy. The lower the size dependent, the smaller the number of available energy values and the discrete function turns into a delta function at zero dimension. Secondly the high surface-to-volume ratio of nanostructures refers normally to the field of surface science. Surface science is the study of physical and chemical phenomena that occur at the interface of two phases, including solid-liquid interfaces, solid-gas interfaces, solid-vacuum interfaces, and liquid-gas interfaces. Some related practical applications are classed as surface engineering.

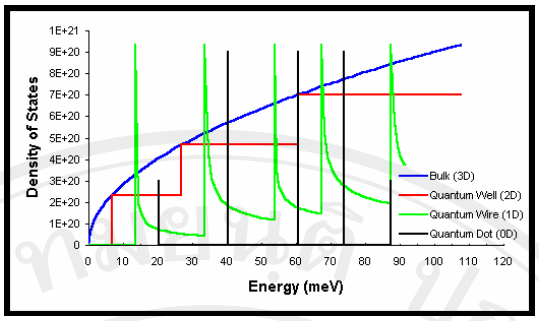


**Figure 1.1** The relation of dimensionality and density of state[(1)].

## 1.2 Basic Properties of Research Materials

### 1.2.1 Copper (II) oxide

Copper (II) oxide (CuO) is one of a few p-type metal-oxide semiconductors with a narrow band gap of 1.2 eV. CuO has a monoclinic crystal structure. It has received much attention due to a wide range of potential applications such as photoconductive, photothermal, catalysis[(2)] and gas sensor[(3)]. Also, CuO is an important building block of most high-temperature superconductors. Now, CuO nanostructures would open new potential applications due to distinctive and novel properties differing from conventional bulk materials. For example, the band gap of CuO nanoparticles (Eg = 2.43 eV) is much larger than that in bulk CuO[(4)]. CuO nanostructures such as nanowires, nanorods, and nanoparticle, etc. can be synthesized by various growth techniques, such as thermal evaporation[(5)], thermal decomposition [(6)] and oxidation[(7),(8)].

CuO nanostructures possess many significant properties, such as the basis of several high temperature superconductors and giant magneto resistance materials, promising solar cells material owing to its photoconductive and photochemical

properties, lithium ion battery, and electron field emission source. CuO nanostructure has two primary applications; ethanol gas sensor and dye-sensitized solar cell. CuO nanostructure sensors have earned attention due to their huge surface-to-volume ratios. Usually, the gas sensing properties of oxide semiconductors strongly depend on the surface of these materials. Thus, gas sensors based on nanostructures are expected to be able to detect gas molecules at lower concentration and exhibit better sensing properties than gas sensors based on bulk material or thin films. Dye-sensitized solar cell (DSSC) is a promising photo energy conversion device. Dye sensitization of metal-oxide wide-band-gap semiconductors such as $TiO_2$, $NiO_2$ and ZnO is a fast growing field for application of solar cell.

In this research, CuO was used as a gas sensor and DSSCs. CuO has been reported for uses in gas sensor applications[2]. The main features of CuO as a semiconductor, have been reported by Koffyberg and co-workers[9], while its transport properties in relation to thermal treatments have been described by Jeong and co-workers[10]. According to the authors, copper ion vacancies can be thermally induced in the oxide. The vacancy charges are compensated by the formation of an equivalent concentration of $Cu^{3+}$, whose extra charge can migrate to one of the proximal $Cu^{2+}$ ions by an activated hopping process. The majority carriers are therefore the holes, as confirmed by thermoelectric power, and the material behaves like a p-type semiconductor. The formation of copper vacancies in $Cu_{1-x}O$ has been observed at temperatures lower than 1000°C, at which the material is, with a good approximation, stoichiometric. The copper deficiency, reported as the x values, was thermogravimetrically determined in the 700–900°C range and was found to be between $1.3\times10^{-2}$ and $3.3\times10^{-2}$ at 700°C. From such data the hole concentration was

estimated and, using conductivity data, their mobility. It should be noted that the reported mobility values were miscalculated. For example, the value of 0.3 $cm^2/V{\cdot}s$ at 394°C for CuO conditioned at 900°C does not fit the conductivity value of 0.03 s/cm and a carrier concentration of $6.6\times10^{19}$ $cm^{-3}$. From the latter data the mobility turns out to be $3\times10^{-3}$ $cm^2/V{\cdot}s$, a more realistic value for a hopping semiconductor. It is also important to note that samples, conditioned at the above temperature range, show an extrinsic behavior for temperatures lower than 400°C[9]. For DSSCs, CuO has been reported for use in dye-sensitized solar cells application such as cathode and p-n junction photoelectrode. The enhancement in the photocurrent with CuO modification is thought to be due to the presence of surface islands of CuO. The overlaid thin surface of CuO has high light absorption characteristics (from ~480 to ~200 nm). This type of absorption enhances the photoactivity of the anode, which leads to the generation of a higher density of carriers.

**1.2.2 Crystal structure and lattice parameters and mechanical properties of CuO**

CuO belongs to the monoclinic crystal system, with a crystallographic point group of 2/m or $C^{2h}$. The space group of its unit cell is $C_{2/c}$, and its lattice parameters are a = 4.6837 (Å), b = 3.4226 (Å), c = 5.1288 (Å), α = 90°, β = 99.54°, γ = 90° [11]. The copper atom is coordinated by 4 oxygen atoms in an approximately square planar configuration. Figure 1.2 shows the monoclinic structure of CuO.

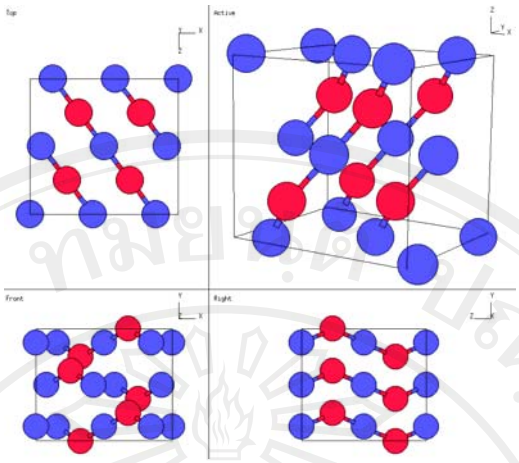

**Figure 1.2** Monoclinic crystal structure of CuO, Oxygen atoms are shown as blue spheres, copper atoms as red spheres[12].

Table 1.1 gives a brief overview of the well accepted and experimentally useful parameters describing the mechanical properties of CuO.

**Table 1.1** List of the general properties of CuO.

| **Properties** | **Volume** |
|---|---|
| Molecular weight | 79.55 |
| Copper weight ratio (%) | 79.89 |
| Oxygen weight ratio (%) | 20.11 |
| Density (kg/m$^3$) | 6310 |
| **Thermal properties** | |
| Malting point ($^o$C) | 1325 |
| Boiling point ($^o$C) | 3980 |
| **Electrical Properties** | |
| resistivity | 6000Ω-cm |
| dielectric constant: | 10.7-18.1 (~300 K) |
| **Bulk Properties** | |
| specific gravity, 20°: | 6.315 |
| Energy gap (eV) | 1.85 (~300 K) |
| Crystal structure | Monoclinic |
| Enthalpy of fusion (kJ/ mol) | 52.30 |

### 1.2.3 Zinc Oxide

Zinc Oxide (ZnO) is one of the metal oxide wide-band gap semiconductors that are commonly used for many applications. It is nearly insoluble in water but soluble in acids and alkalis. It occurs as white hexagonal (wurtzite type) crystal or a white powder commonly known as zinc white. It remains white when exposed to hydrogen sulfide or ultraviolet light. Crystalline zinc oxide exhibits the piezoelectric effect and is thermochromic (it will change color from white to yellow when heated, and back again when cooled down). Zinc oxide decomposes into zinc vapor and oxygen at around 1975$^{o}$C. High-quality single-crystalline ZnO is almost transparent. Zinc oxide occurs in nature as the mineral zincite. It has a band gap about 3.37 eV, and a large exciton binding energy of 60 meV. It also exhibits excellent piezoelectric, chemical, and optical properties for various applications such as ultraviolet–blue emission devices, piezoelectric devices, and gas sensor devices.

### 1.2.4 Crystal structure and lattices parameter and mechanical properties of ZnO

ZnO crystalline in hexagonal wurzite structure as shown in figure 1.3. Along the hexagonal axis, this tetrahedral coordination gives rise to polar symmetry. This polarity is responsible for a number of the properties of ZnO, including its piezoelectricity and ferroelectricity, and is also a key factor in crystal growth, etching and defect generation. The four most common face terminations of wurtzite ZnO are the polar Zn terminated (0001) and O terminated $(000\bar{1})$ faces (c-axis oriented), and the non-polar $(11\bar{2}0)$ (a-axis) and $(10\bar{1}0)$ faces which both contain an equal number of Zn and O atoms. The polar faces are known to posses different chemical and physical properties, and the O-terminated face possesses a slightly different electronic

structure to the other three faces. Additionally, the polar surfaces and the $(10\bar{1}0)$ surface are found to be stable; however the $(11\bar{2}0)$ face is less stable and generally has a higher level of surface roughness than its counterparts. The (0001) plane is also basal.

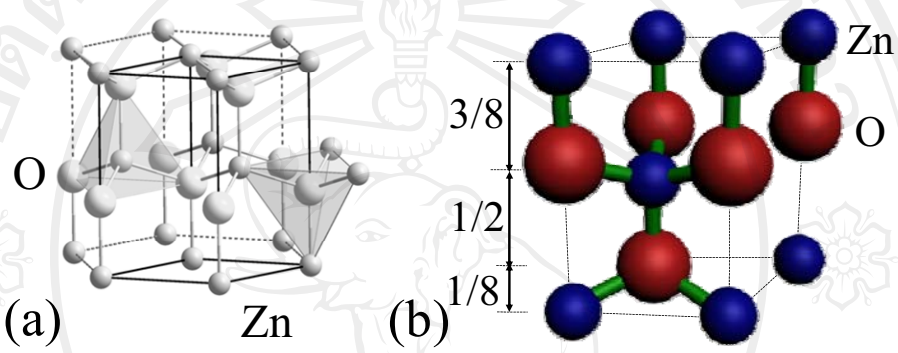


**Figure 1.3** (a) the hexagonal wurtzite structure of ZnO, oxygen atoms are shown as large spheres, zinc atoms as smaller spheres and (b) one unit cell of ZnO structure.

The lattice parameters of the hexagonal unit cell are $a = b = 3.2495$Å and $c = 5.2069$ Å, and the density is 5.605 g cm$^{-3}$. In an ideal wurtzite crystal, the axial ratio $c/a$ and the $u$ parameter (which is a measure of the amount by which each atom is displaced with respect to the next along the $c$-axis) are correlated by the relationship $uc/a = (3/8)^{1/2}$, where $c/a = (8/3)^{1/2}$ and $u = 3/8$ for an ideal crystal. ZnO crystals deviate from this ideal arrangement by changing both of these values. This deviation occurs such that the tetrahedral distances are kept roughly constant in the lattice. Experimentally, for wurtzite ZnO, the real values of $u$ and $c/a$ were determined in the range $u = 0.3817$–$0.3856$ and $c/a = 1.593$–$1.6035$ [(13)].

Table 1.2 gives a brief overview of the well accepted and experimentally useful parameters describing the properties of ZnO.

**Table 1.2** List of the general properties of ZnO [14] .

| **Property** | **Volume** |
|---|---|
| Molecular weight | 81.37 |
| Average atomic weight | 40.69 |
| Average atomic number | 19 |
| Coefficient of thermal expansion | |
| along the c-axis (1/K) | $2.9 \times 10^{-6}$ |
| across the c axis (1/K) | $4.8 \times 10^{-6}$ |
| Density ($g/cm^3$) | 5.6803 |
| Melting point (K) | 2,248 |
| Enthalpy of fusion (kJ/mol) | 52.30 |
| Specific heat at room temperature and constant pressure (J/g.K) | 0.494 |
| Debye temperature extrapolated to 0 K (K) | 416 |
| Static dielectric constant | |
| along the c-axis | 8.75 |
| across the c-axis | 7.8 |
| Optical frequency magnitude | |
| along the c-axis | 3.75 |
| across the c-axis | 3.70 |
| Index of refraction (at the wavelength of 1,400 nm) | |
| Ordinary indices ($n_0$) | 1.984 |
| Extraordinary indices ($n_e$) | 2.001 |

## 1.3 Motivation of Research

CuO has been using for two applications such as gas sensor and DSSCs. For gas sensor application, it is interesting to investigate the effect of CuO nanostructure, which has a huge surface-to-volume ratio, on gas sensing properties. Thus, in this work, the ethanol sensing properties of CuO nanowires prepared by oxidation reaction are examined. The ethanol sensing properties were studied for various ethanol concentrations and working temperatures. For dye-sensitized solar cells application, we synthesize CuO nanostructure with different morphology such as nanowires and thin films by various techniques such as thermal oxidation reaction and thermal

evaporation. Then, the obtained CuO nanostructures are used to fabricate DSSCs and investigate the performance and properties of the DSSCs.

## 1.4 Research objectives and usefulness

### 1.4.1 Objective

- To synthesize CuO nanostructure with different morphology such as nanowires, nanoparticle and thin film by various techniques such as thermal evaporation, oxidation reaction.
- To understand the growth mechanism of nanostructures.
- To fabricate ethanol gas sensor based on CuO nanostructures and characterize gas sensing properties.
- To synthesize CuO nanowires for cathode application in dye-sensitized solar cells.

### 1.4.2 Usefulness

- The research will provide CuO nanostructures for further applications.
- The research will provide ethanol nano sensor for alcohol breath meter.
- The research will provide dye-sensitized solar cell.