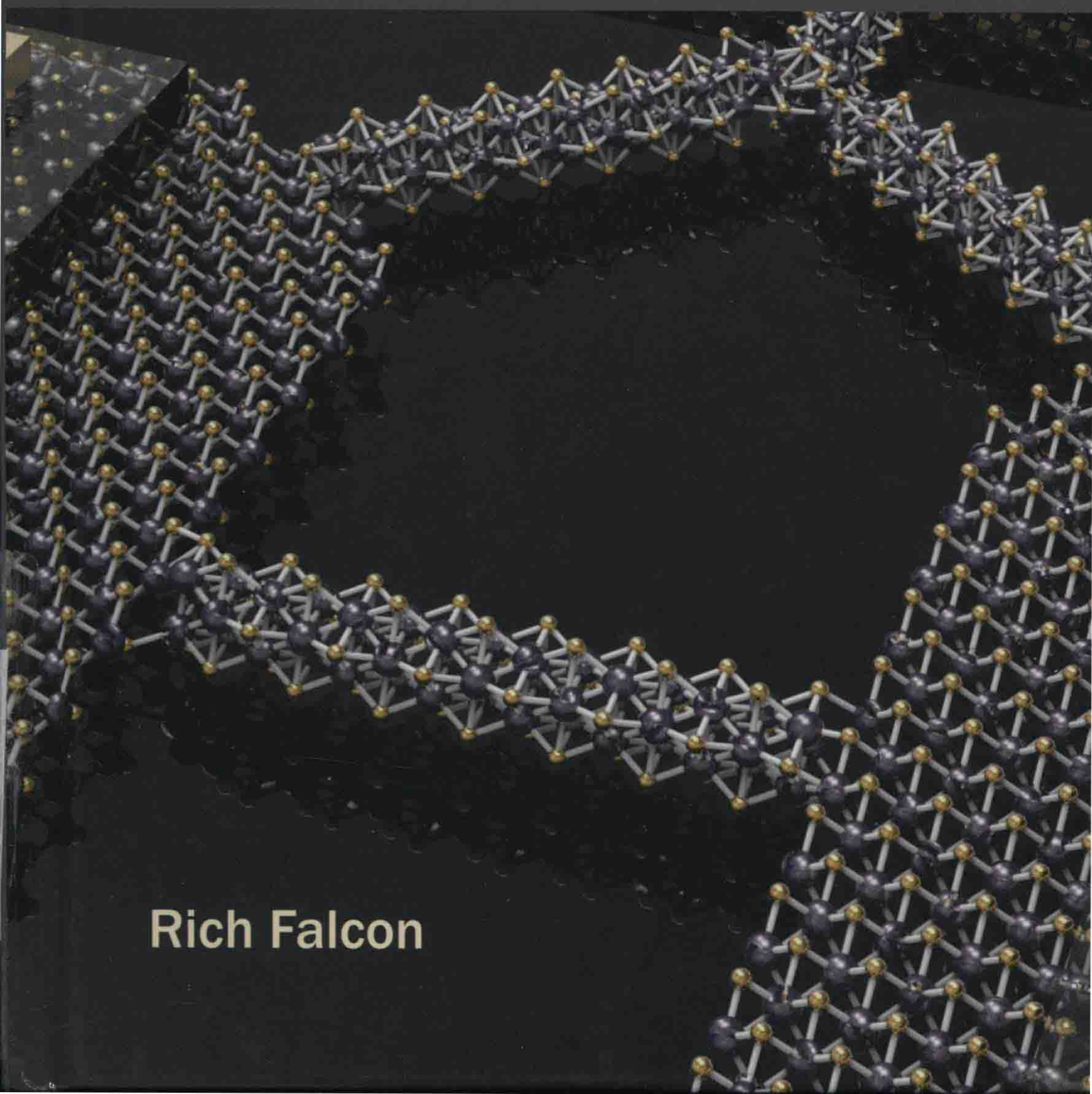
Current Developments in Nanowires



Rich Falcon

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Edited by **Rich Falcon**

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Preface

This book has been an outcome of determined endeavour from a group of educationists in the field. The primary objective was to involve a broad spectrum of professionals from diverse cultural background involved in the field for developing new researches. The book not only targets students but also scholars pursuing higher research for further enhancement of the theoretical and practical applications of the subject.

Structures having diameter of the orders of nanometers are referred as nanostructures. Significant amount of research has been carried out on single dimensional nanoscale structures like nanowires. Miniature sizes bring exclusive properties to nanowires because of quantum captivity. Large surface-to-volume ratios enable high sensitivity to surface effects in nanowires. The distinctive geometrical benefits and properties assist the utilization of nanowires in nanoelectronics. This book is an attempt to provide an advanced assessment of the various uses of different nanowires and related progress in creation and properties characterization. It comprises of discourses on recent developments in metal oxide nanowires, silicon nanowires, carbon based nanotubes and nanowires.

It was an honour to edit such a profound book and also a challenging task to compile and examine all the relevant data for accuracy and originality. I wish to acknowledge the efforts of the contributors for submitting such brilliant and diverse chapters in the field and for endlessly working for the completion of the book. Last, but not the least; I thank my family for being a constant source of support in all my research endeavours.

Editor

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Chapter 1

Metal-Oxide Nanowires for Gas Sensors

Supab Choopun, Niyom Hongsith and
Ekasiddh Wongrat

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1. Introduction

In past decades, gas sensors based on the metal oxide semiconductors (MOSs) have been studied in diverse field for wide applications. A gas sensor is a device that can be used to detect various gas such as ethanol, LPG, CO_2 and CO gases etc. The gas sensors based on MOSs such as SnO_2, TiO_2, WO_3, ZnO, Fe_2O_3, and In_2O_3 have an important role in environmental monitoring, chemical process controlling, personal safety (Q. Wan et al., 2004), industrial process controls, for the detection of toxic environmental pollutants in human health, and for the prevention of hazardous gas leaks, which comes from the manufacturing processes (K. Arshak&I. Gaidan, 2005), wine quality monitoring, and traffic safety (X.F. Song et al., 2009).

The first generation of MOS gas sensors were based on thick films of SnO_2 since 1960s which was firstly reported by Taguchi (E. Comini et al., 2009). The MOS gas sensors have some advantages such as small size, low-power-consumption (E. Comoni et al., 2009), simple construction, good sensing properties (K. Arshak&I. Gaidan, 2005), and high compatibility with microelectronic processing (E. Comini et al., 2002). So, they have rapidly gained attention over the years.

Recently, various morphologies of MOS nanostrcutures such as wire-like, belt-like, rod-like, and tetrapods have been widely investigated for gas sensor applications. It is well-known that the sensitivity characteristics of these sensors strongly depend on the morphology of MOS. Especially, one-dimensional nanostructures such as nanowires, nanobelts, nanoneedles have gained a lot of interest for nanodevice design and fabrication (Wang et al., 2008). The sensors based on MOS nanowires are promising due to feasibility for ultrahigh sensitive sensors or ppb-level sensors. These nanowires can be prepared by various techniques such as pulse laser deposition (PLD), chemical vapor deposition (CVD), thermal evaporation, metal-catalyzed molecular beam epitaxy (CBE) and thermal oxidation technique. Moreover, there are many reports on gas sensor based on the nanowires.

The fundamental mechanism of gas sensing based on MOS depend on the reaction between the surface complexes such as O^-, O^{2-}, H^+, and OH^- reactive chemical species and the gas molecules (reducing/oxidizing gas) to be detected (E. Comini et al., 2009). Thus, it is important to understand the surface reactions between semiconductor surface and target gas for improving the sensing characteristics. Typically, the important parameters in sensor development are sensitivity, selectivity, and stability that called "3S" (E. Comini et al., 2009). However, in this chapter we will mostly discuss on only the sensitivity parameter.

The sensitivity of sensors based on bulk and thin film MOS is typically low. Thus, sensitivity improvement has been extensively studied by using several techniques. The two techniques that commonly used for sensitivity improvement are in the following:

1. *Using nanostructures*

The MOS sensors based on various nanostructures such as nanowires, nanobelts, nanoparticles, nanrods, and nanotubes etc. have been demonstrated to be excellent candidates for ultrahigh sensitivity due to their high surface-to-volume ratio. A large surface-to-volume ratio means that a significant fraction of atoms (or molecules) are much quantity on the surface. So, the reaction between target gas and reactive chemical species (O^-, O^{2-}, H^+, and OH^-) on the surface can extremely occur. A list of MOS sensors with the sensitivity for the different morphologies of ZnO nanostructures is summarized in Table 1. It can be seen that the sensor sensitivity strongly depends on size and morphology of ZnO nanostructures.

2. *Adding noble metal*

The noble metals such as Au, Pt, Pd, and Ag on the surface of MOSs can act as a catalyst to modify surface reactions of MOSs toward sensing gas and result in high sensitivity. The ZnO sensors with noble metal additive are also listed in Table 1.

Usually, the gas sensors based on MOS nanostructures exhibit high sensitivity and sometimes up to a few hundred folds over a conventional MOS sensor at a moderate concentration. On the other hand, the sensors based on a larger size of MOS such as in the form of thin film or micro-tetrapod shows lower sensitivity. Several models have been proposed to explain sensitivity characteristics of MOS sensors and still be a subject of discussion.

There are many reports about gas sensor model that are used to explain sensor response characteristics. Wang and co-workers have proposed a surface-depletion model and a contact-controlled model that are used to describe the sensing mechanism of resistance-type metal-oxide semiconductor sensors (Feng et al., 2005). The surface-depletion controlled model is used to explain the sensing mechanism of semiconducting oxide sensors based on nanocrystal/ nanowire/nanobelt structures, while the contact-controlled model is proposed to explain the contact between the outer ends of the rods. This leads to the formation of many junctions in the sensors that significantly modify the potential barrier of contact between rods. These barriers can control the transport of electrons between the rods resulting in the change of the sensor resistance. Chen and co-workers (Chen et al., 2006) have used space-charge model to explain the sensitivity improvement when the grain size is close to or smaller than the Debye length ($2L_d$).

In this chapter, we investigate the sensing characteristics of the MOS nanowire sensors and present the sensitivity formulas that are developed in order to explain all circumstances of gas sensors based on MOS nanowires. The size and morphology dependences on the sensitivity are explained in terms of the two important parameters including surface-to-volume ratio and depletion layer width. The developed formulas will be discussed and related to the experimental sensing characteristics of ZnO sensors.

Materials	Morphology	Diameter (nm)	Target gas	Sensitivity (ppm)										
				1	10	25	50	100	150	200	300	500	1000	2000
ZnO (Son et al., 2008)	nanowire	20	Ethanol	~16		~40	~54	~62	~70	~70		-	-	
ZnO (Xu et al., 2008)	nanorod	40-80	Ethanol				7.3	-				-	-	
ZnO (Chen et al., 2006)	nanorod	<15	Ethanol		20.5		104.9	176.8		224.2		267.7	-	
ZnO (Bie et al., 2007)	nanorod	10-30	Ethanol		~5		~10	18.29				~32	~42	
ZnO (Li et al., 2009)	nanoneedle	5-10	Ethanol	11	56		116	176		~300		~650	-	
ZnO (Wan et al., 2004)	nanowire	25	Ethanol	~2.5		~8	~16	~33		~47		-	-	
ZnO (Feng et al., 2005)	flowerlike	150	Ethanol	2.2	5.8		11.4	14.6				25.2	30.1	
ZnO (Li et al., 2007)	nanorod	15	Ethanol	4.1	10.7		18.1	29.7				~72	100	
ZnO (Yang et al., 2008)	nanorod	50	Ethanol	10	18		60	100				-	-	
ZnO (Chen et al., 2008)	nanotube	250	Ethanol	2.6			-	24.1		34.8		59.3	-	
ZnO (Choopun et al., 2007)	nanobelt	50-150	Ethanol				7.3		12			21.1	23.2	
ZnO (Hongsith et al., 2008)	nanowire	60-180	Ethanol				-	5.07				9.79	14	14
ZnO (Wongrat et al., 2009)	nanowire	100-500	Ethanol				2	3				5	8	
SnO_2 (Neri et al., 2006)	nanopowder	6-100	Ethanol				~7	~8.6	~10			-	-	
SnO_2 (Lee et al., 2008)	nanorod	<100	Ethanol				-	-				-	~40	
ZnO (Liu et al., 2010)	nanotube	200	H_2				-	2.3				-	-	
ZnO (Bie et al., 2007)	nanorod	10-30	H_2		~5		~7	10.41				~22	~24	
SnO_2 (Zhang et al., 2010)	nanofiber	80-120	H_2				~2	~5				~8	~10	
SnO_2 (Lee et al., 2008)	nanorod	<100	H_2				-	-				-	~10	
SnO_2-Pd (Zhang et al., 2010)	nanofiber	80-120	H_2				~5	~8				~15	~26	

Materials	Morphology	Diameter (nm)	Target gas	Sensitivity (ppm)										
				1	10	25	50	100	150	200	300	500	1000	2000
SnO_2-Pd (Lee et al., 2008)	nanorod	<100	H_2				~33	-				-	~700	
ZnO-Au (Hongsith et al., 2008)	nanowire	60-180	Ethanol				-	6				12	24	37
SnO_2-Pt (Neri et al., 2006)	nanopowder	6-100	Ethanol				~18	26.5	~31			-	-	
SnO_2-Pd (Lee et al., 2008)	nanorod	<100	Ethanol				~15	-				-	~125	
ZnO-Au (Li et al., 2007)	nanorod	15	Ethanol		20.1		41.8	89.5			193.6	-	-	
ZnO-Au (Wongrat et al., 2009)	nanowire	100-500	Ethanol				7	10				20	32	

Table 1. List of MOS sensors with the sensitivity for the different morphologies of ZnO nanostructures.

2. Sensing mechanism and sensitivity parameters

Normally, the gas sensor based on MOS has an optimum operating temperature at high temperature about 250-350°C. When the MOS is heated at lower temperature about 100-200°C, oxygen molecules in the atmosphere are adsorbed on its surface and form oxygen ion molecules by attracting an electron from the conduction band of MOS as shown in the Eq. (1).

$$O_2(gas) + e^- \Leftrightarrow O_2^-(adsorb) \tag{1}$$

At higher temperature, the oxygen ion molecules are dissociated into oxygen ion atoms with singly or doubly negative electric charges by attracting an electron again from the conduction band as shown in Eq. (2) and (3)

$$\frac{1}{2}O_2 + e^- \overset{k_{Oxy}}{\Leftrightarrow} O_{ads}^- \tag{2}$$

$$\frac{1}{2}O_2 + 2e^- \overset{k_{Oxy}}{\Leftrightarrow} O_{ads}^{2-} \tag{3}$$

where k_{Oxy} is the reaction rate constant. The oxygen ions on the surface of MOS are extremely active with the target gas molecule and give up the electrons from the surface back to the conduction band of MOS. The generally chemical reaction between gas molecule and oxygen ions is shown in Eq. (4)