CHAPTER I

INTRODUCTION

1.1 Introduction

Ammonia is a colourless gas with a pungent smell and high toxicity, even low concentration level (ppm). Ammonia is releasing from household cleaners, refrigeration units, fertilizers, explosives, fuels and other chemicals as well as humans and animals from their urine. People are usually exposed to ammonia by breathing air that contains the gas. Moreover liquids that contain ammonia can cause exposure by direct contact with the liquid or by breathing releasing from gas. Larger amounts of ammonia can be detected near farms and industries. Farms have high levels of ammonia due to animal waste storage and the use of liquid ammonia as fertilizer. Industrial sites can release high levels in case of chemical leaks or spills and in sewage treatment plants. Transportation accidents may also release dangerously high amounts of ammonia. Lastly people who keep a lot of pets indoors and do not clean up the animal waste may also source of ammonia.

Ammonia is a toxic gas and suffocating odor. It is recognized as one of the primary irritants to humans. The recommended threshold limit value for human exposure is 25 ppm (18 mg/m^3 of air). Ammonia levels below 1 ppm are not expected to cause health problems. Most people can begin to detect ammonia odors when it is at least 1 ppm. Exposure to more concentrated levels (above 25 ppm) for long term exposure (more than 8 hours) can cause headaches, nausea, and intense burning of eyes, nose, throat, and skin. Exposure to very high levels of ammonia gas can cause serious burns and permanent damage to eyes and lungs. Individuals with asthma and emphysema may be particularly sensitive to ammonia. Therefore, development and fabrication of systems for this purpose are of great contemporary interest. Choice of suitable sensing materials along with efficient microelectronics for the detection system is the key step in such efforts for ammonia.

1.2 Literature Review

There were many principles for measuring ammonia described in literatures. Various sensors were reported for the use in the exhaust pipe of automobiles more than for environmental monitoring with measuring ultra-low concentrations of ambient ammonia. The most frequently used techniques in commercial ammonia detectors were metal-oxide gas sensors, catalytic ammonia detectors, optical ammonia detection techniques and conducting polymer ammonia analyzers.

1.2.1 Metal-Oxide Gas Sensors

Metal-oxide gas sensors, mostly based on SnO_2 were the largest manufactured for ammonia [1]. A lot of research has been done on this type of sensor [1-3], especially in Japan because it was rugged and inexpensive. Many models have been proposed to explain the functionality of these types of sensors [4]. It is well established by now that the gas sensors operate on the principle of conductance change due to chemisorptions of gas molecules to the sensing layer.

A common model is based on the fact that metal-oxide films consist of a large number of grains, contacting at their boundaries [5]. The electrical behaviour is governed by the formation of double Schottky potential barriers at the interface. The height of this barrier determines the conductance. When exposed to a chemically reducing gas, like ammonia, co-adsorption and mutual interaction between the gas and oxygen result in oxidation of the gas at the surface. The removal of oxygen from the grain surface results in a decrease in barrier height [6].

As can be concluded from this model, metal-oxide sensors are not selective to one particular gas. This is a major drawback. Different approaches to make selective sensor systems have been applied [7], like principle component analysis [8], artificial networks, also known as the artificial nose [9, 10] or conductance scanning at a periodically varied temperature [11]. Varying the temperature changes the current density through a Schottky barrier but chemisorption was also a function of the temperature. It is shown that these two effects have different temperature dependency for different gasses. Techniques have been shown to create micromachined isolated hotplates that can be used to miniaturize and integrate these types of sensors on a chip [12-14].

A different approach to make selective metal-oxide gas sensors is by using metals or additives that enhance the chemisorption of specific gases. WO_3 based sensing material is demonstrated to respond to NH_3 and NO [15, 16]. Many materials have been added to this sensing material in order to enhance the sensitivity and the selectivity towards these two gases. Known additives for optimizing the ammonia sensitivity of SnO_2 based ammonia sensors are Pd, Bi and $AlSiO_3$ [17] or Pt and SiO_2 [18].

The lowest ammonia detection limit found in literature is 1 ppm, using WO_3 ammonia sensors with Au and MoO_3 additives. The sensor is operated at an elevated temperature of more than 400 °C [16]. Therefore, metal oxide based sensors still require high operating temperature, which increases running costs. This is a major drawback.

1.2.2 Catalytic Ammonia Gas Sensors

A great number of papers are published about reactivity of catalytic metals to specific gases, for instance ammonia, hydrogen, carbon monoxide or organic vapours [19]. The charge carrier concentration in the catalytic metal is altered by a charge in concentration of the gas of influence. This change in charge carriers can be quantified using a field effect device, like a capacitor or a transistor [20, 21]. The selectivity of these sensors depends on parameters like the used catalytic metal, the morphology of the metal layer and the operating temperature. Ammonia field effect transistors, gasfets, using a palladium gate material have been shown, resulting in a detection limit of 1 ppm.

The catalytic reaction of a metal layer with gaseous ammonia can also be used in combination with a solid-state ion-conducting material to form a gas-fuelled battery. The catalytic reaction at the sensing electrode will cause a change in electrode potential. The resulting potential difference between the electrode and a counter electrode, over the conducting layer, is used to quantify the gas concentration. These sensors are commercially available for many different gasses. The lower detection limit is normally in the low-ppm range and the accuracy is limited. A chemical cell for ammonia is presented in literature based on an anion-exchange membrane with a Cu electrode and an Ag/AgCl counter electrode [22].

1.2.3 Optical Gas Sensors

There are two main optical principles for the detection of ammonia described in literature. The first is based on a change in colour when ammonia reacts with a reagent. With the second principle optical absorption detection is applied as a method to sense gasses.

1.2.3.1 Spectrophotometric Ammonia Detection

Spectrophotometry is technique where a specific reaction causes a coloration of an analyte. The best known example is pH paper, a piece of this paper in a solution. There are many commercially available detection kits for all kinds of ions and dissolved gasses.

There are different coloration reactions in use for dissolved ammonia. Best known is the Nessler reaction. This ammonia detection method is readily available frequently for determining the total ammonia concentration in water, e.g. in aquaria where too high ammonia levels can cause fish to die. The Nessler reagent consists of dipotassium tetraiodomercurate (II) in a dilute alkaline solution, normally sodium hydroxide. This reagent is toxic. There is not much literature about quantitative measurements with this reaction [23], probably because of the disadvantages. Besides the toxicity, a second disadvantage is the formation of the non-soluble reaction product, basic mercury (II) amidoiodide, making the reaction difficult to implement in a miniaturized detection system.

A second coloration method to measure ammonia concentrations in aqueous solutions is the Berthelot reaction. A combination of ammonia, phenol and hypochlorite results in a blue coloration. This reaction uses less dangerous chemicals and the reaction products are all soluble in water. This makes it a suitable technique for integration in miniaturized analysis systems. One drawback of this technique is the rather slow kinetics of the reactions.

1.2.3.2 Optical Absorption Ammonia Detection

Optical absorption spectroscopy is used in the most sensitive and selective ammonia detectors for ambient ammonia. Systems with a detection limit of 1 ppb, that do a full measurement in 1 second, have been reported [24]. Such systems use a laser and a spectrograph. Light travels through air or an ammonia sensitive layer [25, 26]. The spectrum of the light reaching the detector is influenced by either the gas composition or the material characteristics as a function of the gas composition. These systems are used in all kinds of gas analyzers in different application areas. Optical absorbance analyzers that measure multiple gases are commercially available but cost thousands of dollars.

Although very sensitive and selective ammonia detectors are shown, there are some disadvantages when looking at sensor systems for measuring in small volumes. First, the required equipment is very expensive. It has been tried to use inexpensive diode-lasers to overcome this problem but this also resulted in a decrease in sensitivity. Secondly, the sensitivity of absorption spectroscopy is partly determined by the amount of gas between the light source and the detector. For a very accurate analysis the measurement system should be very large. Thus, miniaturization always results in an increase in the lower detection limit. Therefore, this principle is less suited for miniaturized ammonia sensors.

1.2.4 Conducting Polymer Gas Sensors

The measurement principle for ammonia makes use of polymers. Different materials have been reported, like polypyrrole (PPy) [27] and polyaniline (PAni) [28, 29]. The sensing mechanism of PPy films is two-fold: first, there is an irreversible reaction between ammonia and the polymer and secondly, ammonia can reversibly reduce the oxidized form of PPy [30]. The reduction of the polymer film causes a change in the conductivity of the material, making it a suitable material for resistometric [31] or amperometric ammonia detection [27].

Conducting conjugated polymers offer major advantages in the facility with which the recognition elements can be tailored by chemical synthesis and thin film fabrication techniques. Electrically conducting polymers display the extended π-electrons conjugation. The incorporation of the conjugation along the backbone is of foremost importance because it provides a pathway for electrons to migrate along a polymer chain and jump from one chain to another chain. To convert an insulating polymer to a conducting polymer, charge transfer agents, dopants are often require to add electrons into delocalized framework or to remove electrons and leave positive holes. The high electrical conductivity can be accomplished after the doping process, which can be divided into two different processes: the acid doping and the oxidative doping. Several kinds of conducting polymers have been discovered such as polypyrrole (PPy), polythiophene (PT) and polyaniline (PAni). The advantages of conducting polymers compared to inorganic materials used until now are their diversity, their easy synthesis and particularly, their sensitivity at room temperature at low cost.

PPy has been one of the first conducting polymer used in gas sensors [32]. A PPy layer, deposited on raster electrodes, was tested for detecting ammonia and nitrogen dioxide. Its conductance decreased (increased) in the ammonia ambient and increased in nitrogen dioxide ambient. The explanation of this behaviour was based on traditional solid state concepts. PPy conduction being of p-type, the electron-supplying gases (e.g. ammonia) reduce the charge carrier concentration. Thus, on standing in ammonia ambient the conductance drops. In contrast, nitrogen dioxide acts as an acceptor, drawing electrons off the polymer molecules. As this takes place, the majority carrier concentration and polymer conductance increases. The PPy sensor has demonstrated good reversibility of the response to ammonia in the range 100 – 10000 ppm, but the concentration dependence of the response was essentially non-linear. Among the drawbacks of this sensor were low sensitivity and very long response time. Use of PPy sensitive layers in ammonia sensors was also discussed in [32]. These sensors also had low sensitivity and an incomplete desorption of gas molecule, i.e. an incomplete reversibility of the sensor response. More extensive investigations of sensitivity to gases have been carried out in [33].

PAni was found to be a better choice for ammonia gas because of its high sensitivity , reversible response, shorter response time, ease of synthesis and its stability under ambient conditions [34]. PAni can be synthesized via both chemical and electrochemical oxidative polymerizations of aniline in aqueous acid media by variety of oxidizing agents (Figure 1.1). It has a general structure in polyemeraldine base (PAni-EB), which consists of alternating reduced and oxidized repeating unit [35].

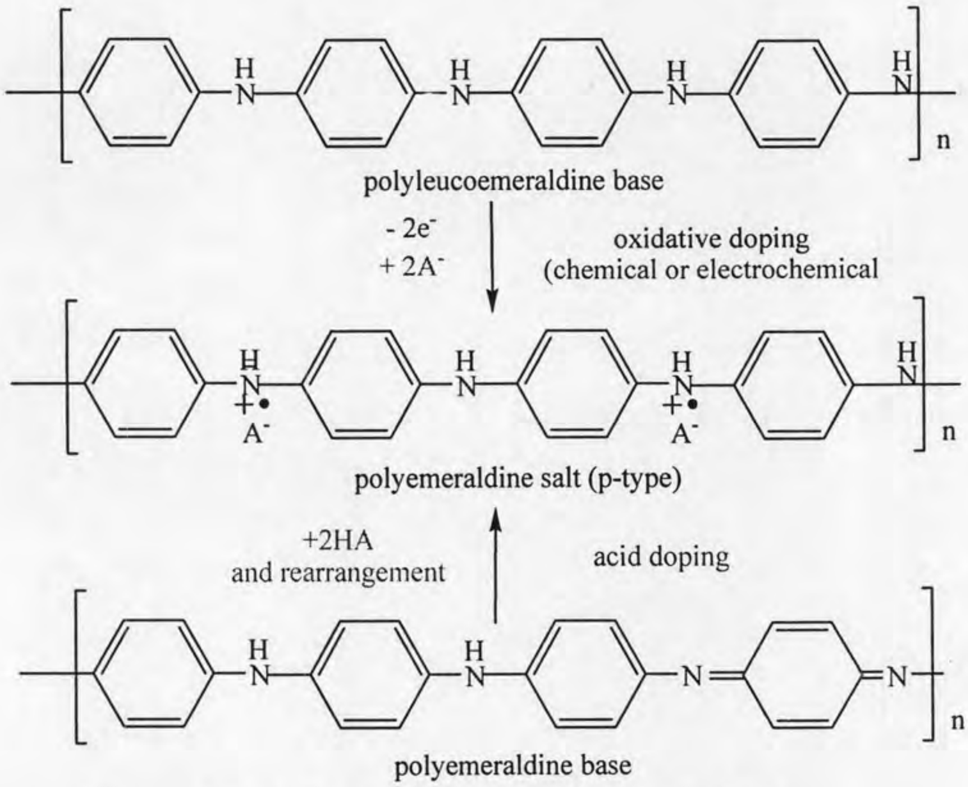

Figure 1.1 Acid doping and oxidative doping of PAni.

Chan et al. [36] synthesized PAni by post-treatment of polyemeraldine base (PAni-EB) with different acids. They report that the phosphoric acid doped PAni had a higher conductivity and thermal stability than hydrochloric acid doped PAni. Palaniappan et al.[37] were prepared five different polyemeraldine salts (PAni-ES) by chemical polymerization of aniline in different acid solution. PAni was hotly treated at various temperatures of 150, 200, 275 and 375°C. Thermal stability of these films was stable up to 250°C and had a three-step weight loss process in thermal analysis. The first step at temperature up to 110°C was related to the loss of water molecule from the polymer chain. In the second step at temperature range 110 – 275°C the loss was due to a small amount of acid evaporated out as a volatile gas. The last step at temperature higher than 275°C corresponded to the oxidative thermal degradation of polymer chain.

In the case of ammonia sensors based on PAni, Jiakun et al reported a high sensitivity to ammonia gas at normal temperature accompanied with low resistive, good selectivity, and reliability. The resistance augmented with the number of electron holes because ammonia molecules acted as donors after being adsorbed, and formed an electric barrier near the surface of the sample. Piletsky et al. [28] reported the use of PAni as the sensitive element for ammonia microsensor. This microsensor was constructed based on a multi-purposed silicon chip with a system of heaters and thermometers. The sensor characteristic of PAni was studied by monitoring the sensitivity of polymer film with a wide range of ammonia gas concentration in the range of 1 – 20000 ppm. A physicochemical model described the changed in the conductivity of PAni with the absorbed ammonia molecules. It was shown that the change in conductivity occurred due to the reversible protonation of PAni molecules in ammonia removal. PAni was used for ammonia sensor because of high chemical stability in oxidizing ambient. Dhawan et al. showed that the leaching of the protonic sites in the doped PAni grafted surface on exposure to aqueous ammonia led to a change in resistance of the polymer. The surface resistance change from 102 to 1010 Ohm. This aspect can be utilized in the designation of chemical sensor for aqueous ammonia.

The major advantage of polymers compared to inorganic materials (specially SnO_2), used until now to measure conductivity variations, is their sensitivity at room temperature. So, Kukla et al. [28] showed a decrease of the polymeric sensor sensitivity when the temperature increase (from 27 to 78 °C), proving that desorption is favored compared to adsorption.

However, as shown with inorganic materials, PAni is sensitive to humidity. According to Collins and Buckley [38], this sensitivity is explained by two kinds of interactions between water molecules and polymer: the formation of hydrogen bonds and swelling in conducting polymer. When heating the polymer, the water effect is totally reversible because the heat breaks the hydrogen bonding between water molecules and polymer chains [28].

Another drawback is the limited life time of the sensor exposed, for example, to ammonia (NH_3) vapor. Different explanations can be put forward [28]. One of them is the natural aging of the organic film, observed even if PAni is not exposed to the gas to be detected. This aging is assigned to a dedoping reaction inside the layer: $\text{PAni-H}^+ + A^- \rightarrow \text{PAni} + \text{HA}$, where HA represents the doping acid molecule. A fraction of HA molecules volatilizes from the layer surface. Another explanation is irreversibility due to accumulation of ammonium residues in the sensitive layer. The layer can be regenerate by heating up to 104-107 °C. NH_4^+ and HA molecules then decompose and release protons. This mechanism allows the regeneration of polyemeraldine salt: $\text{PAni} + H^+ \rightarrow \text{PAni-H}^+$. Finally the limited life time of the sensor can be explained by irreversibility due to an exposition to ammonia vapor for a too long time, more than 1 hour. Even an intense thermal regeneration cannot regenerate it. But if the same sensor is exposed to ammonia vapor for less than 10 minutes, the response is totally reversible.

A lot of studies are dealing with the improvement of sensitivity and selectivity of PAni layer. The parameters showing an influence on these two factors and detailed below are, in particular, the nature of the dopant, the presence and the nature of substituants on aniline ring, the deposition method of sensitive layer, the PAni post-treatment by an organic vapor, the use of threads woven into a fabric mesh as substrate and the use of a composite sensitive film with PAni. Other parameters like electrode geometry [39] and temperature [40] influence the response of gas-sensitive chemo-resistors.

As for the dopant, mineral acid HA (A = Cl^-, HSO_4^-, ClO_4^-) are most often used. When the sensor is kept in an ammonia atmosphere, the layer resistance increases [28, 41, 42]. Note that ammonia is the gas generally detected by PAni layers because of the similar role played by nitrogen atoms of both compounds in the establishment of the coordinence bonding with protons [28, 42].

Recently, a lot of research works deal with the use of a composite film with PAni as sensitive layer. Hosseni and Entezami have studied the response under various gases and organic vapors of layers made from PAni blends with polyvinyl acetate, polystyrene and polyvinyl chloride. Moreover, Cataldo and Maltese describe the preparation of a composite film of PAni (doped with dodecylbenzene sulfonic acid) and polyphenylacetylene and discuss about the choice of the polymer to be added to PAni for gas detection. Ogura et al. have used a composite film of PAni-EB and polyvinyl alcohol to detect CO_2. The CO_2 adsorption leads to an increase of the film conductivity assigned to the transformation of PAni-EB in polyemeraldine salt by the incorporation of carbonate ions formed from CO_2 hydrolysis in the PAni-EB film. Toppare and co-workers [43] have compared performances of PAni films with those of polyaniline/polycarbonate composite films. Matsuguchi et al. [44] have realized ammonia sensors based on polyaniline/polystyrene and polyaniline/polymethylmethacrylate (PMMA) blends. Dopant nature (HCl on bis(2-ethylhexyl) hydrogen phosphate), proportion of each polymer, solvent nature are discussed. The best sensitivities have been obtained with a 7 % w/v PAni/PMMA film doped with bis(2-ethylhexyl) hydrogen phosphate when using toluene as solvent. According to these authors, this kind of blend allows also to improve the solubility of conducting polymers and then their processability. Furthermore, according to Hu et al. [45], the formation of composite films allows PAni to preserve its conductivity even with humidity or heat. Collins and Buckley [38] have studied bilayer of polyaniline/polyethylenimine and polyaniline/fluoropolyol. Finally, Sharma et al. [46] have realized a chloroform sensor based on copper/polyaniline nanocomposite. Besides all measurements of a conductivity change to a direct current, Amrani and co-workers [47-49] under gas effect, a resistance change to an alternative current. The advantage is that a single sensor can discriminate several chemical species. The sensor works at room temperature directly to methanol, acetone or ethyl acetate.

1.2.5 Polymer Blends for Gas Sensor

Over the past few years, attention has been devoted to the use of conducting polymeric composites as a fabricating material for sensor devices [50]. Extensive study on the gas sensing properties of conducting polyaniline composites and polypyrrole composites for various oxidizing and reducing gases with detailed mechanism have been reported [51]. The sensors from these conducting polymeric composites and blends can make in different ways [44, 52, 53]. It has been found that these films are subjected to electron-donating gases such as ammonia.

Sarswati et al. [54] reported about polyaniline-(acrylonitrile-butadiene-styrene) composite film as a sensor material for aqueous ammonia. The resistance change of the composite film on exposure to different concentrations of aqueous ammonia shows its utility as a sensor material. The composite film on exposure to 10^{-4} and 10^{-5} N aqueous ammonia shows well-defined response behaviour and this aspect has been utilized in designing the ammonia sensor.

Matsuguchi et al. [44] reported about the effect of ammonia gas on the electrical conductivity of four kinds of polyaniline-insulating matrix. Polymer blend films were investigated for the purpose of preparing a practical ammonia gas sensor operated near or at room temperature. The electrical conductivity of all blend films measured in N_2 was enhanced above a 2 wt % of composition of PAni. The electrical conductivity decreased by exposure of the blend films to ammonia gas. It was found that the sensing characteristics depended on kind of dopant species, measuring temperature, matrix polymers, and the solvent used for film preparation. Among the considered sensors, the polyaniline–poly (methyl methacrylate) blend film prepared by toluene showed the fastest response and good reversibility, because the porous film was obtained only by this combination.

There are reports of taste sensor fabrication by using a functionalized polymer. Polyvinyl alcohol (PVA) has been modified to fabricate the sensor material [55]. The research work covers polymer membrane preparation, morphology study, structural characterization of the membrane, and study of the taste sensing characteristics. The membrane was prepared by cross-linking polyvinyl alcohol with maleic acid. The cross-linked PVA was phosphorylated with $POCl_3$. Polyvinyl alcohol membranes of suitable thickness were thus prepared with a good threshold sensing value and less swelling in water. The sensor characteristics like temporal stability, response stability, response to different taste substances, and reproducibility of sensing performance were studied.

1.3 The Purpose of the Study

The purposes of this study were the improvement of fabrication, reversibility and reproducibility of ammonia sensor based on PAni. In this work, PAni was prepared by blending with polyvinyl alcohol; citric acid was a cross-linking reagent of PVA and a dopant of PAni. The effect of citric acid dopant, film thickness, temperature and humidity, response time and recovery time, repeatability and linearity of polyaniline-polyvinyl alcohol blended film (PAni-PVA blended film) for ammonia sensing were studied.