CHAPTER I
INTRODUCTION

1.1 Microelectronic Gas Sensor

In recent years, there has been a great interest in the application of micromachined silicon-based devices as solid state gas sensors. Chemical microsensors have an advantage over conventional analytical technology in terms of significantly lower cost, lower power consumption, lower weight, and faster response. These devices are suitable for remote sensing, distributed real-time sensing at multiple locations, and applications requiring portable analytical instrumentation. Thanks to the miniaturization of the sensor surface, only very small amounts of sample are needed. Typical chemical microsensors contain thin films which undergo a change in physical properties when certain gas molecules come in contact with the film surface. A widely used sensing method involves the measurement of thin film conductance changes.

Recent research on gas sensors at the University of Michigan has focused on silicon-based conductivity-type gas detectors based on ultra-thin $Pt/_X$ films supported on selectively-heated micromachined dielectric windows as reported by Johnson, et.al., (1994), U.S. Patent 4,935,387, and Najafi, et.al., (1994). A stress-relieved dielectric window, composed of a sandwich of thermally-grown silicon dioxide (300nm), low-pressure chemical-vapor-deposited (LPCVD) silicon nitride (250nm), and LPCVD silicon dioxide

(700nm), is used to support the sensing film as well as a set of four electrodes for measuring the film conductivity. A boron-doped silicon heater is located under the window. Contacts to the film and the heater are made with Ir/Ti metallization (200nm/25nm), which is stable at high temperatures on the windows. Two boron-doped silicon temperature-sensing resistors are used to monitor the chip temperature within its active area and are interleaved with the heater to provide high thermal coupling and temperature uniformity. Figure 1 shows a schematic cross-section of the device. The thin sensing film (e.g., Pt/TiO_X) is deposited at wafer level and is defined photolithographically using a lift-off process. For films that are not compatible with the final silicon etch used for window formation and die separation, a selected area CVD method has been developed to deposit a larger variety of sensing film materials as reported by Majoo, et.al. (1996). The silicon heater located directly underneath provides the capability to rapidly heat just the film region, so that thermally activated CVD can be confined to a geometrically well defined area in the center of the sensing device.

One of the challenges encountered in micro-CVD of platinum films is that during the vapor deposition, the backside of the window which contains the boron-doped silicon heater, is also getting hot. Electrically conducting metal films forming on the backside of the gas sensor window tend to short out the contacts for the heater. One method to avoid this problem is to protect the backside of the sensor with a thermally stable, insulating layer of polymer, for example, polyimide.

N. Najafi, K. D. Wise and J. W. Schwank, IEEE trans. Elec. Dev., 41(10), pp. 1770-77, 1994

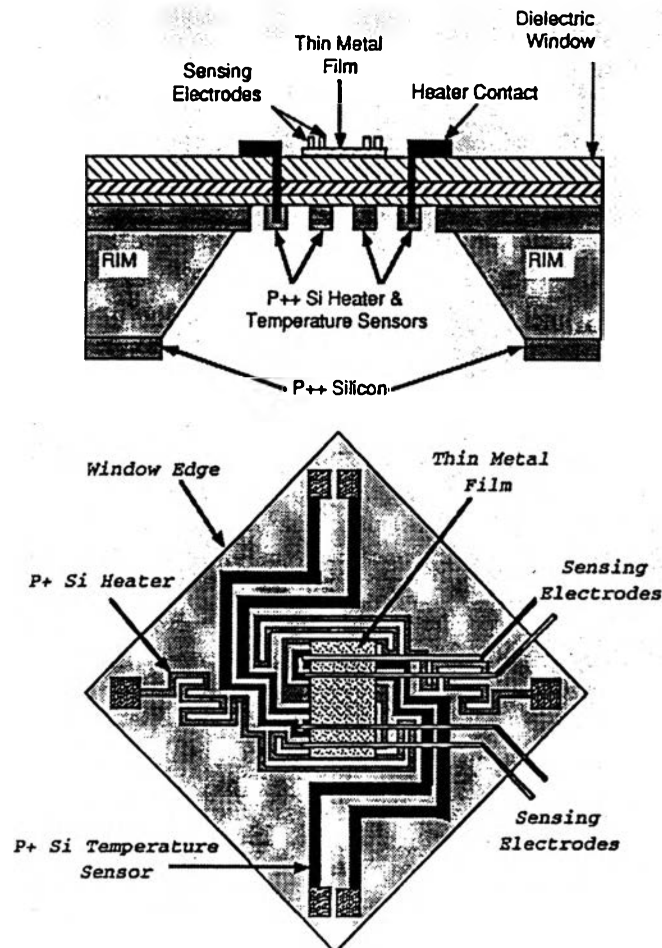

Figure 1 Top view and cross section of the gas detector structure.

1.2 Objective

The objective of this research project is to evaluate suitable polymers and appropriate polymer film coating techniques for this application. The desired specifications for the protective polymer coating include:

(1) thermal stability up to at least 400°C

(2) a thermal expansion coefficient similar to silicon

(3) good adhesion to doped as well as undoped silicon over the entire temperature range of interest

(4) good conformal coverage

(5) electrically insulating polymer

(6) low surface tension and low viscosity in a form of polymer solution which is necessary to make it possible to provide a smooth coating on the backside of the sensor

1.3 Polyimide Films

Polyimides can fulfill almost all of the requirements listed above for an ideal protective polymer coating. Polyimides have found wide application in the microelectronics industry. Polyimides exhibit excellent thermal, mechanical and electrical properties.

As a first step towards applying the polyimide films on fully micromachined sensing devices, this work has focused on suitable methods for casting of very thin polyimide films on silicon wafers, 1×1 cm in size. The properties of these polyimide films have been characterized by a variety of experimental techniques. The outcome of these experiments will set the stage for future development of methods for deploying polyimide films on the small regions on the backside of the micromachined sensing devices.

1.3.1 Basic Chemical Reaction

The conventional method of polyimide films formation is known as the two-stage synthesis. Typically the first stage is dealt with a poly(amic

acid) synthesis by adding a tetracarboxylicdianhydride to a solution of diamine in polar aprotic solvent. The poly(amic acid) solutions are obtained from the polycondensation of dianhydride and diamine. The properties of poly(amic acid) solutions and films gradually change under long term storage conditions at room temperature. The viscosity of the solutions, molecular weight, strength, and elasticity of the polymer films gradually decrease to a certain limit corresponding to the equilibrium between chain decomposition and resynthesis, The second stage of polyimide is so-called imidization, in which the cyclodehydration of poly(amic acid) takes place when the solutions are treated at elevated temperature. At high temperature, the polyimide chains start to cross-link. This is indicated by a loss in solubility even in sulfuric acid. The increases in elasticity and modulus of polyimide at elevated temperature due to the loss in water and imidization take place as shown in Figure 2.

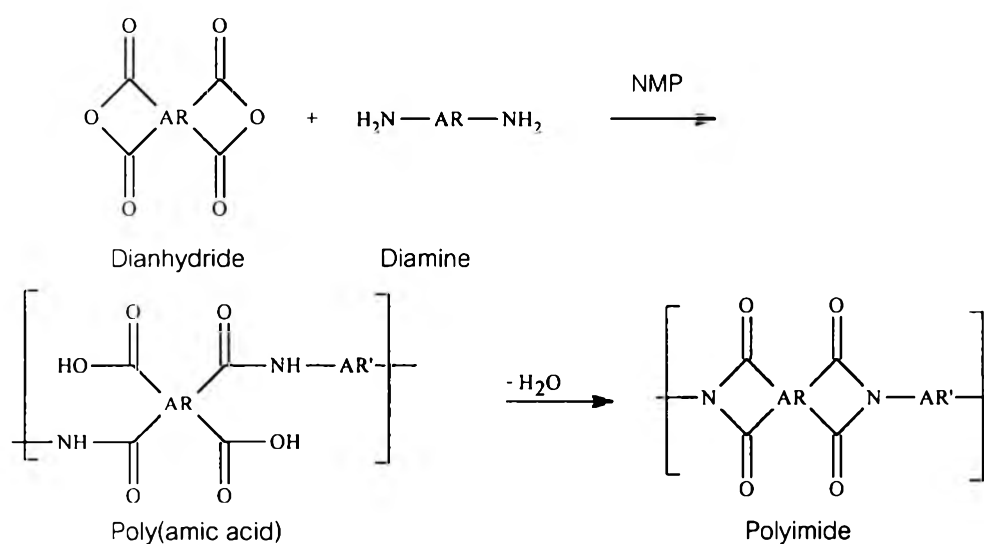

Figure 2 Mechanism of polyimide formation.

1.3.2 Degree of Imidization

The degree of imidization or cyclization of poly(amic acid)s can be evaluated by several methods. For example, IR spectroscopy gives various

degrees of imidization calculated from the band ratio method by Laius, et.al (1967). Numata, et.al (1982). and Eumi Pyun, et.al. (1989) used the UV spectroscopy to study the kinetics and mechanisms of thermal imidization of poly(amic acid). They found that the solid-state imidization rate was initially faster than in dilute solution due to the catalytic effect of the neighboring amic acid group but leveled off due to vitrification, in other words, the decomposition of poly(amic acid)s back to the anhydride and diamine precursors occurred.

1.3.3 Thermal Expansion Behaviors

The term coefficient of linear thermal expansion (CTE) is used for studying the behavior of the polymer films as defined in Equation (1)

$$\alpha = \frac{1}{l}\left(\frac{\partial l}{\partial T}\right)_P \qquad (1)$$

where l is length, T is temperature and P is pressure. The CTE of a polyimide is a function of the backbone and morphology which is strongly influent by molecular orientation. In the microelectronics application as a passivation layer or the coating films, the matching of CTE of the coating films and the substrates is very important. Delaminating, wrapping and bending of the films to the substrate will occur if the CTE of a polymer and substrate material, is mismatched. Many scientists studied the relationship of the CTE and other parameters which would affect this property. Lin and Bidstrup (1993) reported the effect of surface material on the orientation of polyimide films, the processing condition which is the important factor for controlling the expansion behavior of the film. Numata, et.al. (1982) investigated the CTE of both poly(amic acid) and the complete imidized polyimide film by

thermomechanical analysis. Corburn and Pottiger, (1994) reported an in-plane and out-of-plane CTE which affected the stress of polyimide especially for the thin films on the substrate.

1.3.4 Polyimide Structure in Thermal Treatment

The conformation of the polyimide chain after thermal treatment play a role in highly crystalline texture. Jwo-Huei Jou, et.al (1991) studied the in-plane and out-of-plane X-ray diffraction pattern of polyimide film as a function of curing temperature. The molecular order of polyimide film was higher than that of the precursor poly(amic acid). The orientation of the thin film can be also evaluated from the diffraction pattern. It was found that the arrangements of polyimide chain were more orderly in the rigid chain structure than the flexible one, especially in the film plane direction.

1.3.5 Surface Topology of Polyimide

The surface profile of the thermal treatment polyimide film is another important aspect for a good protective film. Excellent insulating properties of the polyimide films indicate the uniformity of the film surface, not only on the film coated on bare silicon wafers, but also on the pattern substrates of the gas sensor array. The macroscopic profile of the film surface will be taken from optical microscopy. In a smaller scale, the high resolution instrument. for example, the atomic force microscope, will be used. In particular regions, the molecular arrangement of the thin films can be observed which will be advantageous for the gas sensor with a small pattern inside.

1.3.6 Solid Dielectric Properties

One of the objectives for fabrication of protective polymers is to obtain good electrical insulating layers. These insulating materials or

polyimide films in this experiment are used to isolate components of an electrical system which come from the CVD process. In general, the heat resisting properties of polyimide films are acceptable with the high insulation resistance. Thermal breakdown is a break down caused by internal heating in the insulation due to dielectric loss. Insulating materials are not perfect capacitors and they do have internal energy losses. The quality of the insulation is often measured in terms of how small these losses are, with the loss factor tanδ, where (90-δ) is the phase angle between voltage and current for a sample of the material; commonly used as the parameter to assess the losses. This energy dissipated within the insulation will cause heating, and electrical insulators are usually poor thermal conductors, so a significant rise in the temperature of the insulation will be produced. In some circumstances, the internal losses may increase as the temperature increases and a thermal runaway situation results. The temperature of the material will rise, losses will increase and the temperature will rise further until the material fails. Thermal breakdown is most likely to occur in power cables operated beyond their power rating, polymer operating near their softening points, or in high frequency applications.

Capacitance techniques are important at frequencies from 1 Hz to 1 MHz as reported by Goldfarb et.al. (1987). In these techniques the electric fields are nearly normal to the sample plane. The difficulty with these measurements is the minimizing of fringing field effects. The fringe field is usually partially eliminated by measuring the capacitance with and without sample and subtracting the results. Guard electrodes also can protect from fringing the field by minimizing field bending near the probe edges. Dielectric constant measurements using capacitor fixtures are influenced by air gaps between the capacitor and the sample. An air gap at the interface will make the calculated value low for the real part of the dielectric constant. The impedance

analyzer is capable to obtain the material measurements of thin materials from 1 to 500 MHz (from the Hewlett Packard Product note no., 1994). The impedance measurement is made directly by sampling the current and voltage. This technique is valid in the frequencies range where lumped circuit parameters can be used. For materials with low real dielectric constant, uncertainties range from 2 to 10 %.