Abstract

In the present work fabrication and characterization of gridded gate $Pt/SiO_2/Si$ MOS sensor has been proposed for detection of hydrogen and hydrogen containing gases. In the recent years the several impacts on the environment due to the burning of fossil fuels have attracted the modern world for clean energy source; Hydrogen is being used as a clean energy source in many industries like chemical, food, semiconductor, petroleum, research laboratory etc. It is well known fact that hydrogen is inflammable, explosive as well as hazardous gas. In order to have a safe working environment its continuous monitoring is required. Hydrogen sensors form an integral part of any such systems incorporating hydrogen as a fuel. Over the past several years much attention has been focused on the development of micro gas sensors for various applications ranging from detection of toxic gases to monitoring of the gases that are used in industries for manufacturing purposes. The demand for better environmental control and safety and that with less expensive way has commenced the increased activities in the field of solid state gas sensors. Single crystal silicon has remained the best choice among the researchers for sensor fabrication due to its intrinsic mechanical stability and the feasibility of integrating sensing and the signal processing electronics on the same substrate. Though silicon has the highest material cost per unit area, but this cost often be offset by the small feature size possible in a silicon implementation. Furthermore, the reduction in terms of power consumption and the mass production capabilities of the IC technology based on the silicon are the main driving force for fabrication of Si- based IC compatible sensors. Keeping this in view, Silicon has been used as substrate throughout the present work.

In the present investigation, hydrogen detection properties of platinum gate MOS structure on <100> silicon has been carried out. The characterization and performance study of the fabricated MOS sensors having SiO_2 as insulator have been investigated. An effort has also been made to improve the performance of Pt-gate MOS sensor by using plasma treated SiO_2 instead of conventional thermally grown SiO_2.

Chapter 1 has been designed for Introduction and literature survey to justify the scope of the thesis outlined.

Chapter 2 has described the theory of MOS sensor.

In Chapter 3 the detail fabrication procedure of gridded gate Pt/SiO_2/Si MOS sensor has been discussed. The various fabrication and measurement facilities available in the laboratory are also discussed in this chapter. The gridded Pt gate MOS capacitor sensor has been fabricated on 3” P type <100> (1-6 Ω-cm) Si wafer. For fabrication of Pt/SiO_2/Si MOS capacitor, the wafer was thoroughly cleaned using standard technological cleaning procedures used in silicon technology as described in section 3.4.2 of Chapter 3. The SiO_2 layer (about 100 Å) was grown by dry thermal oxidation of silicon wafer in the oxidation furnace at 500 ^{0}C. Subsequently, photolithography technique was used for retaining front side oxide and removing back side oxide (as mentioned in section 3.4.4). After that a platinum film of 350 Å has been deposited on front face of silicon wafer by thermal evaporation method. A standard mask is used to form gridded gate structure. Details of fabrication steps have been described in this chapter.

Chapter 4 describes the device characterization of gridded gate Pt/SiO_2/Si MOS sensor. The surface morphology of the deposited Pt film has been investigated through SEM study. It is revealed from the SEM analysis that Pt microstructures are uniformly distributed throughout the film surface. Moreover, the film surface comprising cracks and microporous structures which may lead to improved sensing behaviour of the device. Further, the surface morphology and porous nature of the deposited Pt gate structure has been investigated through AFM study. AFM study confirms the microporous nature of the metal gate film.The C-V and G-V response of the sensor as a function of signal frequency with varying concentration of test gases (H_2, NH_3, CH_4 and H_2S) have been carried out in air ambient. The interface trap charges have been evaluated towards test gases (H_2, NH_3, CH_4 and H_2S) at different frequencies (15 KHz, 25 KHZ and 50 KHz) and concentrations both. The sensitivity ‘S’ of the sensor has been defined by [S%= $((C_{air} - C_{gas})/C_{air})$x100= $(\Delta C/C)$x100] in terms of capacitance and [S% = ((G_{pi}-G_{pgas})/G_{pi})x100] in terms of conductance.

In Chapter 5 of this thesis, we have reported the effect of RF oxygen plasma on the response of gridded gate Pt/SiO2/Si MOS sensor. In the present work, 9 samples of gridded Pt/SiO_2/Si MOS capacitors were fabricated on P type <100> 3” Si substrate out of which one sample (S1) was non plasma treated and 8 samples (S2-S9) were

plasma treated. The fabrication process of non plasma treated gridded gate Pt/SiO_2/Si MOS sensor has been described in section 3.4 of Chapter 3.

Initially, all the samples were thoroughly cleaned using standard technological cleaning procedure used in silicon technology. A SiO_2 film of ~120 Å was grown by the dry thermal oxidation method by keeping all 9 samples in oxidation furnace at 850 ^{0}C for a specified time in O_2 and N_2 ambient atmosphere. For optimization of plasma treatment, these 8 samples (S2-S9) were divided into two sets (each set containing four samples). Each set was exposed to RF oxygen plasma with different RF power (40W and 50W, respectively) and all four samples of each set were exposed to RF plasma for different duration of time (2min., 4min., 8min., and 12min.). The PECVD system was operated in capacitive coupled mode at 13.56 MHz. For the required gridded gate structure photolithography using lift off technique has been performed. The surface analysis has been carried out by Atomic Force Microscopy (AFM). Comparative study between plasma treated and non plasma treated sensors has been carried out in terms of sensitivity (%) vs bias voltage and fixed charge density variation with various concentrations. The details of work are presented in Chapter 3, 4 and 5. Following are the conclusions which have been extracted from this work.

1. A Gridded Pt gate MOS sensor has been developed for detection of hydrogen and hydrogen containing gases to obtain better sensitivity and tested at H_2, NH_3, CH_4 and H_2S.
2. The C-V and G-V measurements have been carried out at various frequencies (15 KHZ, 25 KHz and 50 KHz) and test gas concentrations both. It has been found that MOS sensor exhibited better sensitivity at lower frequency.
3. The low frequency conductance method provides the better information of interface trap charge density and it has been found that interface trap charge density increases with decrease in frequency. Further, it has also been observed that interface trap charge density decreases with increase in hydrogen concentration.
4. The porous structure of the Pt gate film as detected from SEM and AFM studies (Fig. 4.1 and 4.2, Chapter 4) may be the reason of enhanced sensitivity towards hydrogen.

5. The sensitivity of gridded gate $Pt/SiO_2/Si$ MOS sensor for hydrogen (~**90**% in terms of change in capacitance) is found to be more as compared to other gases NH_3 (85%), CH_4 (45%) and H_2S (68%) and the sensitivity (in terms of change in conductance) is found to be maximum for H_2 (45.66%) as compared to other test gases NH_3 (27.88%), CH_4 (23.4%), and H_2S (14.7%)
6. It has been observed that gridded gate $Pt/SiO_2/Si$ MOS sensor is much more sensitive to very low concentration of NH_3 (25 ppm), CH_4 (50 ppm) at room temperature (27 ^{0}C) and for H_2S (10 ppm) at 120 ^{0}C temperature.
7. The high sensitivity of gridded $Pt/SiO_2/Si$ MOS structure to H_2 is attributed to the side wall diffusion of H_2 molecules, improved diffusion and dissociation of hydrogen molecules, increase in surface area of Pt film due to large porosity found in the film, high polarizability of SiO_2, spill-over mechanism and increase in fixed charge density with H_2 concentration.
8. To the best of authors' knowledge it is for the first time that the gridded gate $Pt/SiO_2/Si$ MOS sensor has been fabricated and it is found that sensitivity of gridded gate MOS structure improves drastically towards H_2 and H_2 containing gases.
9. The gridded gate $Pt/SiO_2/Si$ MOS sensor has been fabricated with plasma treated SiO_2 film and tested towards H_2. The goal of this experiment was to study the combined effect of gridded gate structure with RF oxygen plasma treated SiO_2 on C-V characteristics, fixed charge density, (%) sensitivity, grain size and average roughness and it is found that sensitivity towards hydrogen improves drastically for oxygen plasma treated sensors. The sensitivity (in terms of change in capacitance) was found to be maximum for S4 sensor (~91%) as compared to non plasma treated sensor (S1) (~73%).
10. The sensitivity was found to be increased with increase in plasma exposure time. The maximum sensitivity has been recorded ~91% in case of 40 W, 8min. plasma exposure. This is due to large grain size, large porosity and more roughness found in the film. However, in case of 50 W, when plasma exposure duration exceeds beyond 4 min., the oxide surface gets severely damaged (confirmed by AFM study) probably due to ion sputtering of the SiO_2 surface may take place. The comparative study among the plasma treated and non plasma treated sensors has also been discussed.