Chapter 5

SAW Sensor for Detection of Oxidizing Gas (NO₂) using SnO₂ Sensing Layer

In the present chapter, surface acoustic wave (SAW) gas sensor has been exploited for the detection of oxidizing gas such as NO₂. SnO₂ thin films deposited under optimized conditions have been identified as an efficient sensing layer for the room temperature detection of NO₂ gas. Sensitivity, cross-selectivity and stability of the sensor structure for the detection of NO₂ gas have been investigated. An effort has been made to explain the involved sensing mechanism towards NO₂ detection in the light of the properties of sensing layer.
5.1 Introduction

As we have described earlier in chapter 3, semiconducting metal oxides offer specific advantages as sensing layer over other materials like polymers. It has been reported that these sensors become selective and sensitive on properly choosing the sensing layer structure [Haridas et. al., 2008]. ZnO thin films grown under optimized conditions are shown (chapter 3 and 4) to be offering excellent properties as sensing layer for efficient and selective detection of liquor ammonia (a reducing gas). Various metal oxides like SnO$_2$, WO$_3$, CuO, CeO$_2$, ZnO etc have been widely exploited for the detection of different gases/vapors using a number of detection techniques. Pi chart shown in figure 5.1 clearly shows a relative comparison of different oxide materials used for gas-sensing application. It may be clearly seen from the Pi-chart (Fig.5.1) that amongst all metal oxide materials [Haridas et. al., 2010], tin oxide is the most widely investigated material (37%) for detection of various gases, followed by ZnO (10%). SnO$_2$ is extensively used in the form of porous ceramics, thick films, thin films, nanostructures etc. for the fabrication of semiconductor gas sensors. Surprisingly not much efforts have been made towards development of SnO$_2$ sensing layer based SAW gas sensors which, as explained earlier, may provide a better platform for wireless detection of toxic gases at room temperatures.

NO$_2$ is an oxidizing and a highly toxic gas. Sensors capable of detecting NO$_2$ gas in trace levels at room temperature are essentially required. A lot of work has been carried out by various workers on fabrication of conductivity based semiconductor gas sensors for detection of NO$_2$ gas, mostly utilizing SnO$_2$ as the sensing element [Sharma et. al., 2011; Santos et. al., 1997; Shi et. al., 2004; Dieguez et. al., 2000; Yamada et. al., 2003]. However, high operating temperatures and limited sensor performances are the critical issues to be taken care of. In the present work, focus is on the development of SAW gas sensor for detection of an oxidizing (NO$_2$) gas. As a first step, the sensors prepared for the detection of liquor ammonia using ZnO sensing layer (Chapter 3) were tested for NO$_x$ gas but no appreciable response was obtained. Hence, another material used extensively for the gas detection i.e. SnO$_2$ was utilized as a sensing layer for detecting NO$_2$ gas, because of its excellent gas sensing properties and high stability. A brief review on the SnO$_2$ material and its properties desired for gas sensing application is presented in following sections.
Figure 5.1: Relative comparison of different metal oxides used for gas-sensing application [Haridas et. al., 2010]

5.2 Structure and Properties of Tin Oxide (SnO\textsubscript{2})

SnO\textsubscript{2} or stannic oxide is a wide band gap compound semiconductor with good chemical and mechanical stability. It has one stable phase in the form of rutile structure [Haridas et. al., 2008]. A representation of the SnO\textsubscript{2} unit cell is given in figure 5.2, where red spheres represent oxygen atoms and grey sphere represent Sn atoms.

Figure 5.2: Schematic of SnO\textsubscript{2} unit cell [Haridas, et. al., 2010]

The rutile structure has a tetragonal unit cell with a space-group symmetry of P42/mmm. The crystalline structure contains Sn atoms in octahedral coordination and oxygen atom in a planar three coordination (Fig.5.2). Table 5.1 gives a brief summary of the physical properties of SnO\textsubscript{2}.
Table 5.1: Physical properties of SnO₂ [Batzill et. al., 2005]

<table>
<thead>
<tr>
<th>Stable Phase</th>
<th>Tetragonal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice Parameters</td>
<td>( a = 4.737 \text{ Å} ) and ( c = 3.186 \text{ Å} )</td>
</tr>
<tr>
<td>O-O distance</td>
<td>4.6646 Å</td>
</tr>
<tr>
<td>O-Sn distance</td>
<td>3.7662 Å</td>
</tr>
<tr>
<td>( c/a )</td>
<td>0.673</td>
</tr>
<tr>
<td>Density at 300 K</td>
<td>6.9-7.0 g/cm³</td>
</tr>
<tr>
<td>Melting point</td>
<td>1630 °C</td>
</tr>
<tr>
<td>Refractive Index</td>
<td>2.008</td>
</tr>
<tr>
<td>Static Dielectric constant</td>
<td>9.86</td>
</tr>
<tr>
<td>Energy Band Gap</td>
<td>3.6 eV</td>
</tr>
</tbody>
</table>

SnO₂ is n-type extrinsic semiconductor due to the presence of large amount of native defects related to oxygen vacancies which creates the donor level (0.03 and 0.14 eV) below the conduction band (related to single and double ionization of oxygen vacancies) [Haridas et. al., 2010]. SnO₂ possess excellent capability of exchange of oxygen from the atmosphere due to natural non-stoichiometry which makes it most suitable material for gas sensing application. The early report on gas-sensing properties of SnO₂ was given by Windischmann et. al., (1979) where successful detection of carbon monoxide was demonstrated. Since then a large number of reports came which were related to the application of SnO₂ thin films for the detection of different gases [Batzill et. al., 2006; Chen et. al., 2005; Ma et. al., 2012; Gopel et. al., 1995; Yamazoe et. al., 1991]. In the present work SnO₂ thin films have been utilized as a sensing layer in SAW device for the detection of NO₂ gas.

5.3 Need for NO₂ Gas Sensors

Nitrogen dioxide is the chemical compound with the formula NO₂. Nitrogen dioxide is a paramagnetic bent molecule with \( C_{2v} \) point group symmetry. It is one of the form out of several nitrogen oxides. NO₂ is an intermediate product in the industrial synthesis of nitric acid, millions of tonnes of which are being produced every year [Internet 10].
This reddish-brown toxic gas has a characteristic sharp, biting odor and is a prominent air pollutant. One potential source is fuming nitric acid, which spontaneously produces NO$_2$ above 0 °C. The most important sources of NO$_2$ include internal combustion engines, thermal power stations, butane gas heaters and, to a lesser extent, pulp mills [Internet 16]. The excess air required for complete combustion of fuels in these processes introduces nitrogen into the combustion reactions at high temperatures and produces nitrogen oxides (NO$_x$). Limited production of NO$_x$ demands the precise control on the amount of air used in combustion. In households, kerosene heaters and gas heaters are the sources of nitrogen dioxide. NO$_2$ is also produced by atmospheric nuclear tests, and is responsible for the reddish color of mushroom clouds. It is also produced naturally during electrical storms. The term for this process is "atmospheric fixation of nitrogen". The rain produced during such storms is especially good for the garden and agriculture as it contains trace amounts of fertilizer. Nitrogen dioxide is a large scale pollutant, with ground level concentrations in some rural areas is around 30 µg/m$^3$ [Internet 17]. Nitrogen dioxide plays a role in atmospheric chemistry, including the formation of troposphere ozone.

A 2005 study by researchers at the University of California, San Diego, suggests a link between NO$_2$ levels and Sudden Infant Death Syndrome [Internet 17]. Symptoms of poisoning (lung edema) tend to appear several hours after inhalation of a low but potentially fatal dose of NO$_2$ [Internet 18]. Further, exposure to low concentrations (4 ppm) of NO$_2$ anesthetizes the nose, thus creating a potential for over exposure [Internet 18]. There is evidence that long-term exposure to NO$_2$ at concentrations above 40–100 µg/m$^3$ may decrease the lung functioning and increase the risk of respiratory symptoms [Internet 17]. Nitrogen dioxide causes a range of harmful effects on the lungs, increased inflammation of the airways, worsened cough and wheezing, reduced lung function, increased asthma attacks, greater likelihood of emergency department and hospital admissions, increased susceptibility to respiratory infection, such as influenza [Internet 19]. Further, NO$_2$ gas can cause various other problems such as smog and acid rain [Sharma et. al., 2011]. Hence, development of efficient sensors preferably operating at room temperature for wireless detection of NO$_2$ gas is important.
In the present work, an effort has been made towards wireless and room temperature detection of NO$_2$ gas using SAW gas sensors.

### 5.4 Review of NO$_2$ SAW Sensors

Few efforts have been made by various workers towards detection of NO$_2$ gas using SAW sensors. A brief review of the reports on SAW gas sensor for NO$_2$ gas is presented in Table 5.2. As can be seen from the Table 5.2, different coatings have been utilized as sensing layer for the detection of NO$_2$ gas using SAW sensors and most of the initial reports are based on the utilization of copper phthalocyanine (CuPc) film. CuPc film is reported to be yielding good sensitivity allowing sub ppm and even ppb level detection of NO$_2$ gas. However, the major issue with the usage of CuPc film is the high response and recovery time (~ few minutes), besides high operating temperature [Rugemer et. al., 1999; Becker et. al., 1996]. Further, the effect of other interferants on the performance of SAW sensor performance was not studied. The polymer thin film of polypyrrole was also used as a sensing layer for detection of NO$_2$ gas by Mashat et. al., (1998) and Yan et. al., (2012). However, stability of the SAW sensor was poor, and response and recovery time was still high (in minutes) which is the major drawback for the realization of a fast sensor [Mashat et. al., 1998; Yan et. al., 2012]. Dewan et. al., (2007b) deposited TeO$_2$ thin films on the surface of SAW devices (with LiNbO$_3$ substrate) to make them temperature stable SAW gas sensor and demonstrate the detection of NO$_2$ gas at room temperature [Dewan et. al., 2007b]. However in the report selectivity issue was not even accounted [Dewan et. al., 2007b]. The other reports highlight the importance of metal oxides or bilayer structure of polymer and metal oxide as sensing layer for NO$_2$ gas detection (Table 5.2). However, the obtained sensing results were not promising due to slow response and recovery speeds and lack of selectivity studies besides high operating temperature (Table 5.2). This highlights the importance of further studies towards development of SAW gas sensor having suitable chemical interface layer to obtain efficient sensing response characteristics towards NO$_2$ gas. In the present work, SnO$_2$ thin films have been utilized as a sensing layer for the efficient, fast and wireless detection of NO$_2$ gas at room temperature using SAW gas sensors.
Table 5.2: A brief review on different sensing layer coatings investigated for SAW gas sensor for the detection of NO₂ gas

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Sensing Layer</th>
<th>Frequency (MHz)</th>
<th>Gas Concentration</th>
<th>Response time</th>
<th>Recovery time</th>
<th>Frequency shift/Amplitude shift/Phase shift</th>
<th>Operating Temperature and Interferants</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>ST-Quartz</td>
<td>Polypyrrole/TiO₂</td>
<td>123.5</td>
<td>10-100 ppm</td>
<td>&gt;1 min</td>
<td>&gt; 1 min</td>
<td>30-110 Hz</td>
<td>RT¹, interfering with H₂S</td>
<td>Yan et. al., 2012</td>
</tr>
<tr>
<td>YX-LiNbO₃</td>
<td>InOₓ</td>
<td>138.2</td>
<td>0.5-8.5 ppm</td>
<td>-</td>
<td>-</td>
<td>73-91 kHz</td>
<td>RT, small interference with H₂</td>
<td>Kiriakidis et. al., 2012</td>
</tr>
<tr>
<td>41° YX LiNbO₃</td>
<td>ITO</td>
<td>440</td>
<td>0.61-5 ppm</td>
<td>&gt; 90 s</td>
<td>&gt; 5 min</td>
<td>51.5 °/ppm</td>
<td>240 °C, selectivity not studied</td>
<td>Lim et. al., 2011</td>
</tr>
<tr>
<td>128° YX-LiNbO₃</td>
<td>WO₃</td>
<td>101.7</td>
<td>0.5-10 ppm</td>
<td>-</td>
<td>-</td>
<td>5-75 kHz</td>
<td>RT, selectivity not studied</td>
<td>Wen et. al., 2010</td>
</tr>
<tr>
<td>36° YX LiTaO₃</td>
<td>Polypyrrole/ZnO</td>
<td>100</td>
<td>2.1 ppm</td>
<td>133 s</td>
<td>298 s</td>
<td>5 kHz</td>
<td>RT, selectivity not studied</td>
<td>Mashat et. al., 2008</td>
</tr>
<tr>
<td>LiNbO₃</td>
<td>InOₓ/ ZnO</td>
<td>136</td>
<td>510 ppb-8.5 ppm</td>
<td>-</td>
<td>-</td>
<td>75-95 kHz</td>
<td>(100-273 °C), selectivity not studied</td>
<td>Ippolito et. al., 2005</td>
</tr>
<tr>
<td>YZ-LiNbO₃</td>
<td>CuPc</td>
<td>363</td>
<td>0.05-0.2 ppm</td>
<td>-</td>
<td>-</td>
<td>0.5-3 db</td>
<td>150 °C, selectivity not studied</td>
<td>Beck et. al., 1999</td>
</tr>
<tr>
<td>YZ-LiNbO₃</td>
<td>CuPc</td>
<td>360</td>
<td>0.1-0.8 ppm</td>
<td>&gt; 5 min</td>
<td>&gt; 5 min</td>
<td>0.05-0.30 dB</td>
<td>Selectivity not studied</td>
<td>Rugemer et. al., 1999</td>
</tr>
<tr>
<td>128° YX-LiNbO₃</td>
<td>WO₃</td>
<td>42</td>
<td>20-100 ppm (100-200 °C)</td>
<td>&gt; 2 min</td>
<td>&gt; 5 min</td>
<td>20-140 ppm</td>
<td>100-250 °C, interferes with CH₄ and CO</td>
<td>Penza et. al., 1997</td>
</tr>
<tr>
<td>LiNbO₃</td>
<td>CuPc</td>
<td>170-370</td>
<td>0.05-0.2 ppm</td>
<td>~ few minutes</td>
<td>~ few minutes</td>
<td>0.08-0.34 dB</td>
<td>100 °C, selectivity not studied</td>
<td>Becker et. al., 1996</td>
</tr>
<tr>
<td>131° YX LiNbO₃</td>
<td>CuTsPc</td>
<td>61.3</td>
<td>0-20 ppm</td>
<td>~10 min (12 ppm)</td>
<td>~40 min (12 ppm)</td>
<td>128 Hz/ppm, saturate above 25 ppm</td>
<td>Not interfering with CO</td>
<td>Yuquan et. al., 1994</td>
</tr>
<tr>
<td>Substrate</td>
<td>Sensing Layer</td>
<td>Frequency (Mhz)</td>
<td>Gas Concentration</td>
<td>Response time</td>
<td>Recovery time</td>
<td>Frequency shift/Amplitude shift/Phase shift</td>
<td>Operating Temperature and Interferants</td>
<td>Reference</td>
</tr>
<tr>
<td>--------------------</td>
<td>---------------</td>
<td>-----------------</td>
<td>-------------------</td>
<td>---------------</td>
<td>---------------</td>
<td>--------------------------------------------</td>
<td>---------------------------------------</td>
<td>---------------------------------------</td>
</tr>
<tr>
<td>ST-Quartz</td>
<td>PbPc and CuPc</td>
<td>600</td>
<td>5 ppm</td>
<td>&lt; 2 min.</td>
<td>Few minutes</td>
<td>2.5-0.8 kHz</td>
<td>120 °C, selectivity not studied</td>
<td>Schickfus et. al., 1997</td>
</tr>
<tr>
<td>ZnO/ SiO₂/Si</td>
<td>CuPc</td>
<td>52</td>
<td>50-250 ppm</td>
<td>-</td>
<td>-</td>
<td>0.4-0.6 kHz</td>
<td>150 °C, selectivity not studied</td>
<td>Nieuwenhuizen et. al., 1994</td>
</tr>
<tr>
<td>ST-Quartz</td>
<td>CuPc</td>
<td>100</td>
<td>20-100 ppm</td>
<td>1-6 min</td>
<td>1.5-7 min</td>
<td>1-6 kHz</td>
<td>Selectivity not studied</td>
<td>Rebiere et. al., 1993</td>
</tr>
<tr>
<td>-</td>
<td>CuPc/PbPc</td>
<td>600 MHz</td>
<td>1-40 ppm</td>
<td>4 hrs</td>
<td>7 hrs</td>
<td>2 kHz/ppm</td>
<td>75 °C, selectivity not studied</td>
<td>Rapp et. al., 1992</td>
</tr>
<tr>
<td>ZnO/ SiO₂/Si/PCPVDA</td>
<td>CuPc</td>
<td>70</td>
<td>50 ppm</td>
<td>-</td>
<td>-</td>
<td>6.2 kHz</td>
<td>150 °C, selectivity not studied</td>
<td>Nieuwenhuizen and Nederlof, 1992</td>
</tr>
<tr>
<td>LiNbO₃</td>
<td>TeO₂</td>
<td>38 MHz</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>RT, selectivity not studied</td>
<td>Dewan et. al., 2007b</td>
</tr>
</tbody>
</table>

* RT = room temperature
5.5 Growth of SnO$_2$ Thin Films

SnO$_2$ thin films have been deposited on the surface of SAW resonator devices by rf sputtering technique. As mentioned earlier, the fabrication of good quality sensitive thin film plays a vital role in obtaining the reliable and enhanced response characteristics of a SAW gas sensor, which in turn depends on the growth kinetics and demands careful optimization of deposition parameters. A disc of Sn metal (4 inch dia. and 99.99% pure) was used as target for the deposition of SnO$_2$ thin films. Prior to deposition of SnO$_2$ thin film, substrates (ST-quartz, glass, Si) are thoroughly cleaned by standard wet chemistry using soap solution, acetone, trichloro ethylene, isopropyl alcohol followed by drying in jet of dry N$_2$. Si wafers were treated separately using the standard RCA cleaning procedure. The processing parameters used in the present study for the deposition of SnO$_2$ thin film are listed in Table 5.3.

**Table 5.3: Deposition parameters of SnO$_2$ thin film by rf sputtering**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Target</td>
<td>4&quot; dia. Sn metal disc (99.99% pure)</td>
</tr>
<tr>
<td>Target to substrate distance</td>
<td>6.5 cm</td>
</tr>
<tr>
<td>Sputtering power</td>
<td>200 W</td>
</tr>
<tr>
<td>Gas composition</td>
<td>100 % O$_2$</td>
</tr>
<tr>
<td>Sputtering Pressure</td>
<td>8 to 30 mT</td>
</tr>
<tr>
<td>Substrate temperature</td>
<td>Room temperature</td>
</tr>
</tbody>
</table>

For the efficient propagation of SAW waves, the electrical conductivity of the sensing layer should be as low as possible. SnO$_2$ thin films deposited with lower oxygen content in reactive gas mixer of Ar and O$_2$ were found to be highly conducting in comparison to that deposited in 100% O$_2$ ambient. The high electrical conductivity may be attributed to the presence of large amount native defects related to oxygen vacancies in the as-deposited SnO$_2$ thin film grown under oxygen deficient sputtering ambient. SnO$_2$ coated SAW resonator devices were utilized as frequency determining element in the Colpitt’s oscillator circuit. It is important to point out that the SAW resonator coated with SnO$_2$ thin film grown under low oxygen content (< 100%) in reactive sputtering gas (Ar + O$_2$) exhibit highly unstable oscillator frequency. However, the SnO$_2$ thin film deposited under 100% O$_2$ ambient on the surface of SAW resonator device results in a
stable SAW oscillator with resonant frequency $f_s$. Therefore SnO$_2$ thin film as sensing layer was deposited only in 100 % O$_2$ ambient. Further deposition of SnO$_2$ sensing thin film layer was performed at room temperature and sputtering pressure was optimized to obtain enhanced response characteristics of SAW gas sensor towards NO$_2$ gas. The thickness of SnO$_2$ sensing layer was varied from 30 to 150 nm.

5.6 Characterizations of SnO$_2$ Thin Films

5.6.1 Structural Characterization (XRD Analysis)

XRD patterns obtained for the as grown SnO$_2$ thin films of different thickness (30 to 150 nm) deposited by rf sputtering technique on ST-quartz substrate is shown in figure 5.3. The SnO$_2$ thin films were deposited under a growth pressure of 20 mT. The broad and well defined reflections were observed at about $2\theta = 33.7^\circ$ and $51.6^\circ$ corresponding to (101) and (211) planes, respectively, in the XRD pattern of the SnO$_2$ thin film (Fig.5.3). The observed XRD peaks are in good agreement to the corresponding reported values for rutile structure of SnO$_2$ [Ihokura et. al., 1994; Miao et. al., 2003], confirming the growth of polycrystalline SnO$_2$ thin film. Further it can be seen that with increase in thickness of SnO$_2$ film (30 to 150 nm) the intensity of the XRD peaks increases (Fig.5.3). A shift in XRD peak towards higher angle ($2\theta$) was observed with increase in thickness of SnO$_2$ thin film (Fig.5.3).

![Figure 5.3: XRD spectra of SnO$_2$ thin films of different thickness](image_url)
The crystallite size of the SnO₂ thin film was evaluated by fitting the width of (101) reflection (the dominant peak) using Scherrer's formula and its variation as a function of film thickness is shown in figure 5.4. The crystallite size was found to decrease from 15 nm to 10 nm with increase in thickness of SnO₂ film from 30 nm and 150 nm. Similar results of decrease in crystallite size with increase in thickness of SnO₂ thin films is also observed by Salunkhe and Lokhande (2008) and Xu et al., (1991) have studied the effect of crystallite size of SnO₂ thin film on the gas sensing characteristics, and reported that smaller crystallite size is advantageous for gas sensing application. Since gas sensing is a surface dominating phenomena, the large surface to volume ratio of sensing layer on the surface of SAW gas sensor is preferred. The small crystallite size of (10 to 11 nm) sensing SnO₂ thin film at higher thickness (≥ 120 nm) provides large grain boundaries and more surface area for interaction with the target NO₂ gas molecules.

![Figure 5.4: Variation of crystallite size as a function of thickness of SnO₂ thin films](image)

Lattice constants (a and c) of the as-grown SnO₂ thin films are estimated from XRD peaks and are shown in figure 5.5 as a function of the thickness of SnO₂ thin film. The estimated values of lattice constants ‘a’ and ‘c’ for SnO₂ thin film in the thickness range 30 to 150 nm are found to be slightly higher than the corresponding bulk values [a = 4.738 Å and c = 3.187 Å (JCPDS 41-1445)] indicating that the lattice of SnO₂ thin film is in a state of elongation and the unit cell is under stress. The lattice constant ‘a’ was found to approach the corresponding bulk value for higher thickness (≥ 120 nm) of
SnO$_2$ thin film (Fig. 5.5). However, the lattice constant ‘c’ of SnO$_2$ film approaches the corresponding bulk value for 50 nm thickness (Fig. 5.5) and there after starts deviating again at higher thickness (>100 nm) The obtained results are in good agreement to the reports available on SnO$_2$ thin films deposited by other workers [Montilla et. al., 2004].

**Figure 5.5:** Variation of lattice constant with the thickness of the SnO$_2$ thin films

The XRD pattern of SnO$_2$ thin films deposited at different sputtering pressures (8 to 30 mT) and of fixed thickness (120 nm) is shown in figure 5.6.

**Figure 5.6:** XRD pattern of SnO$_2$ thin films deposited at different sputtering pressures (8 to 30 mT)
Only two XRD peaks corresponding to (101) and (211) planes of the rutile structure of SnO$_2$ were observed in the XRD pattern of all as deposited SnO$_2$ thin films, indicating the growth of polycrystalline thin films. It can be noted from figure 5.6 that the relative intensity of (101) XRD peak for SnO$_2$ thin film decreases with increase in growth pressure from 8 to 30 mT. It is also important to identify that the crystallite size of the SnO$_2$ thin film decreases from 11 nm to 8 nm with increase in sputtering pressure from 8 to 30 mT.

5.6.2 Surface Morphologies

The surface morphology of the SnO$_2$ thin films deposited at different sputtering pressures is studied by scanning electron microscopy (SEM) and the micrograph of their surface are shown in figure 5.7. The surface morphology of all deposited SnO$_2$ thin films was fine having uniformly distributed nanosize crystallites. The size of crystallites of SnO$_2$ thin film was seen to decrease with increase in the growth pressure (Fig.5.7), and is in agreement with the XRD studies discussed earlier (Fig.5.6). The surface of SnO$_2$ thin film deposited at low pressure (8 mT) was seen to be having porous and rough microstructure (Fig.5.7).

![SEM micrograph of the surface of SnO$_2$ thin films deposited at different sputtering pressures (8 to 30 mT) on ST-X quartz substrate.](image)

**Figure 5.7**: SEM micrograph of the surface of SnO$_2$ thin films deposited at different sputtering pressures (8 to 30 mT) on ST-X quartz substrate.
However, surface morphology becomes smooth, and densely packed microstructure (Fig.5.7) was formed for SnO$_2$ thin films deposited at moderate sputtering pressure (10 to 20 mT). It is interesting to note from figure 5.7 that the microstructure of SnO$_2$ thin film deposited at much higher sputtering pressure (30 mT) again becomes porous and rough.

The surface roughness of all deposited SnO$_2$ thin film was studied using a surface profiler (Dektek 150), and its variation as a function of sputtering pressure is shown in figure 5.8. It may be noted from figure 5.8, that the surface roughness of SnO$_2$ thin film decreases significantly from 16 to 10 nm with slight increase in growth pressure from 8 mT to 10 mT. However, roughness of the SnO$_2$ thin film was found to increase from 11 nm to 18 nm (Fig.5.8), at higher growth pressure (20 mT to 30 mT). The observed variation of surface roughness of SnO$_2$ thin film is in agreement with the SEM analysis discussed earlier. The roughness of SnO$_2$ thin film was found to decrease with increase in thickness.

![Figure 5.8: Variation of surface roughness of SnO$_2$ thin film with the sputtering pressure (8 to 30 mT)](image)

5.6.3 Optical Properties

FTIR Spectroscopy

FTIR spectroscopic measurements were carried out on SnO$_2$ thin film deposited on KBr substrate because it is chemically non-reactive and possesses no lattice absorption bands in the useful region of the IR spectrum i.e. transparent in the IR region. SnO$_2$ thin films were
deposited under similar processing conditions on the KBr pellets and FTIR spectra were recorded. Figure 5.9 shows the FTIR spectra of the as-grown SnO\(_2\) thin films of 120 nm thickness and grown under different sputtering pressures (8 to 30 mT). The absorption band observed at around 600 cm\(^{-1}\) corresponds to the SnO\(_2\) lattice mode [Bentley et. al., 1968] thus confirming the formation of SnO\(_2\) thin film (Fig.5.9). The absorption bands observed at around 1379 and 1094 cm\(^{-1}\) (Fig.5.9) are assigned to the surface –OH groups attached directly to the surface oxygen of the SnO\(_2\) thin film [Milligan et. al., 1963], and the absorption band at 1633 cm\(^{-1}\) is attributed to H-O-H in plane deformation. No significant shift in the position of SnO\(_2\) absorption band (600 cm\(^{-1}\)) was observed with increase in sputtering pressure (Fig.5.9), indicating that the bond strength of the Sn-O bond is same for all SnO\(_2\) thin films deposited under varying growth pressures (8 to 30 mT).

**Figure 5.9:** FTIR spectra of the as grown SnO\(_2\) thin films deposited at different sputtering pressures (8 to 30 mT)

**UV-Visible Optical Transmission**

The optical transmission spectra of all as-grown SnO\(_2\) thin films of different thickness were recorded over the wavelength range of 200 to 1100 nm, and are shown in figure 5.10. A sharp ultraviolet cut off characteristic corresponding to fundamental adsorption edge at a wavelength of about 320 nm was observed. Transmission of the deposited SnO\(_2\) thin films was found to be more than 80% in the visible region (Fig.5.10) showing...
growth of films with good optical quality. The optical transmission of the SnO$_2$ thin film was found to decrease slightly (85% to 80%) with increase in thickness of SnO$_2$ thin films from 30 nm to 150 nm.

![Figure 5.10](image1.png)

**Figure 5.10:** *UV visible transmission spectra of the SnO$_2$ thin films for different thicknesses (30 to 150 nm)*

Optical band gap of the SnO$_2$ thin films were calculated from the intercept on energy (hv) axis obtained by extrapolating the linear portion of the Tauc plot of $(\alpha h\nu)^2$ versus photon energy (hv) as shown in figure 5.11.

![Figure 5.11](image2.png)

**Figure 5.11:** *Tauc plot of $(\alpha h\nu)^2$ versus hv for 120 nm thin SnO$_2$ film*
Estimated value of band gap for as-grown SnO\textsubscript{2} thin films of thickness 30 to 150 nm is found to be in the range 3.8 to 3.9 eV, and is slightly lower than the corresponding values (3.95 to 4.30 eV) reported by other workers for SnO\textsubscript{2} thin films grown by various techniques [Spence et. al., 1967; Sharma et. al., 2011]. Further the value of optical band gap was found to decrease slightly from 3.9 eV to 3.8 eV with increase in thickness of SnO\textsubscript{2} thin film from 30 nm to 120 nm. The estimated values of band gap for all prepared SnO\textsubscript{2} thin films is found to be slightly higher than the corresponding bulk value (3.6 eV), and may be attributed to the small crystallite size (10 to 15 nm) of the SnO\textsubscript{2} thin films. The UV-Visible transmission spectra of SnO\textsubscript{2} thin films deposited at different sputtering pressures (8 to 30 mT) is shown in figure 5.12. The optical transparency of the SnO\textsubscript{2} thin films deposited at different sputtering pressure was almost same (~ 82%). Also no significant change in the value of band gap (3.9 eV) is observed for the SnO\textsubscript{2} thin films deposited at different sputtering pressures (8 to 30 mT).

![Figure 5.12: UV visible transmission spectra of the SnO\textsubscript{2} thin films deposited at different sputtering pressures](image)

5.6.4 Electrical Properties of SnO\textsubscript{2} Thin Films

The electrical properties of SnO\textsubscript{2} thin films of different thicknesses (30 to 150 nm) were studied using Hall measurement in Van der Pauw arrangement. Figure 5.13 show the variation of resistivity of SnO\textsubscript{2} thin films measured at room temperature as a function of
film thickness. Resistivity of SnO\(_2\) thin films was found to decrease from \(2 \times 10^7\) Ω-cm to \(4 \times 10^5\) Ω-cm with increase in thickness from 30 to 150 nm. The observed decrease in resistivity may be attributed to the increase in defects related to oxygen vacancies in SnO\(_2\) thin film with increasing film thickness. The oxygen vacancies in SnO\(_2\) thin film act as donor levels below the conduction band and results in an increase in the electrical conductivity with increase in film thickness.

![Graph showing variation of resistivity of SnO\(_2\) thin films as a function of thickness](image)

**Figure 5.13**: Variation of resistivity of SnO\(_2\) thin films as a function of thickness

The variation of charge carrier concentration and carrier mobility of all deposited SnO\(_2\) thin film as a function of thickness is shown in figure 5.14. SnO\(_2\) thin film was exhibiting n-type semiconducting behavior with electrons as majority charge carriers. The mobility of charge carrier decreases from 236 to 40 cm\(^2\)/V-sec with increase in thickness of SnO\(_2\) thin film from 60 nm to 120 nm and thereafter shows a significant increase in mobility to a value of about 5580 cm\(^2\)/V-sec (Fig.5.14) at higher film thickness (150 nm). The observed decrease in the mobility of SnO\(_2\) thin films is attributed to the decrease in crystallite size from 15 nm to 11 nm with increasing film thickness from 30 nm to 120 nm (Fig.5.4). The decrease in crystallite size results in an increase in the grain boundaries which in turn increase the scattering centres for the charge carriers in SnO\(_2\) thin film and hence reduces the mobility. However, the enhancement in carrier mobility observed for higher thickness (150 nm) of SnO\(_2\) thin
film (Fig.5.14) may be attributed to the improved crystallinity of deposited thin film (Fig.5.3). The concentration of charge carriers in SnO$_2$ thin film was found to increase from $2.61 \times 10^8$ to $2.72 \times 10^{11}$ cm$^{-3}$ with increasing film thickness from 60 nm to 120 nm (Fig.5.14) and thereafter decreases to a value of $1.97 \times 10^9$ cm$^{-3}$ with further increase in SnO$_2$ film thickness to 150 nm. The observed increase in carrier concentration may be due to increase in oxygen vacancies in the SnO$_2$ thin film with increasing thickness, thereby creating more donor levels in the forbidden gap and giving large concentration of charge carriers in the conduction band of SnO$_2$.

![Figure 5.14: Variation of mobility and carrier concentration of SnO$_2$ thin films as a function of thickness](image)

5.7 Response of SnO$_2$/SAW Sensors for NO$_2$ Gas

5.7.1 Effect of Film Thickness

SnO$_2$ thin films of varying thickness from 30 nm to 150 nm were deposited on the surface of SAW resonator having resonance frequency, $f_0 = 433.8$ MHz. The resonance frequency ($f_s$) of SAW resonator was found to reduce with the deposition of sensing SnO$_2$ thin films. The difference in resonance frequency of SnO$_2$ coated SAW oscillator (SnO$_2$/SAW) and bare SAW oscillator (reference) are plotted in figure 5.15 as a function of the thickness of SnO$_2$ thin film. It may be noted from figure 5.15 that the value of resonance frequency of SAW resonator decreases from $f_0$ to $f_s$ with integration of SnO$_2$ thin film. The shift in resonant frequency ($f_0 - f_s$) was found to increase from
860 kHz to 39.35 MHz with increase in thickness of SnO$_2$ thin film from 30 nm to 150 nm (Fig. 5.15). The observed decrease in value of $f_s$ (from $f_o$) is due to the mass loading effect of deposited SnO$_2$ thin film on the surface of SAW resonator. As discussed in chapter 3, the SnO$_2$ based SAW gas sensor was used in differential frequency oscillator configuration where one branch comprises of oscillator circuit having SnO$_2$/SAW device in the feedback loop and other branch comprises of bare SAW resonator (reference device) in feedback loop of oscillator. The differential frequency of two oscillator circuit [$(\Delta f)_a = f_o - f_s$] was monitored by a frequency counter. The value of this differential frequency of SAW gas sensor without any interaction with target (NO$_2$) gas molecules is considered as a base line frequency [$(\Delta f)_a$]. The value of base line frequency for dual SAW oscillator having SnO$_2$ thin film of varying thickness from 30 nm to 150 nm are shown in figure 5.15.

![Figure 5.15: Variation of baseline frequency of SAW sensor in dual oscillator configuration with the thickness of SnO$_2$ sensing layer](image)

The interaction of target (NO$_2$) gas with the surface of SAW resonator having SnO$_2$ sensing layer will result in the shift in its resonant frequency from $f_s$ to $f'_s$ and the output of SAW dual oscillator circuit will be [$(\Delta f)_g = f_o - f'_s$]. The response of SAW gas sensors in differential oscillator configuration will be the differential frequency shift i.e. $S_s = (\Delta f)_g - (\Delta f)_a$. It may be noted that before carrying out the sensing response measurement of SAW sensors towards NO$_2$ gas, the baseline of the dual oscillator
circuit was set to zero frequency \([(\Delta f)_a = 0]\). The response characteristics of SAW sensors having SnO$_2$ sensing thin film of different thickness (30 nm to 150 nm) with exposure to 20 ppm NO$_2$ gas are shown in figures 5.16 (a) to (e) as a function of time. During interaction of NO$_2$ gas molecules with SAW sensor having 30 nm thin SnO$_2$ coating, differential frequency of dual oscillator \([(\Delta f)_g]\) decreases by 16 kHz from baseline \([(\Delta f)_a = 0]\) i.e., a negative shift in differential frequency is observed \((-S_a)\) as shown in figure 5.16(a). The SAW gas sensor was found to recover the value of initial base line frequency slowly after removal of NO$_2$ gas (Fig.5.16a). A negative shift in differential frequency \((-S_a)\) of about 140 kHz was observed for 60 nm thin film SnO$_2$ coated SAW gas sensor (Fig.5.16b) with interaction of 20 ppm NO$_2$ gas. The response \((-S_a)\) of SnO$_2$/SAW gas sensor increases significantly to 16.6, 30.0 and 34.0 MHz respectively (Fig.5.16(c) to (e)) with further increase in the thickness of sensing SnO$_2$ thin film to 90, 120 and 150 nm. The obtained results clearly indicate that the sensing response of SnO$_2$/SAW gas sensor depends significantly on the thickness of sensing SnO$_2$ layer and increases with increase in thickness of SnO$_2$ thin film.

Variation of response time and recovery time of all the prepared SAW sensors having sensing SnO$_2$ thin films of different thicknesses is shown in figure 5.17 for 20 ppm NO$_2$ gas. It can be seen from the figure 5.17 that response time decreases from 12 to 2 seconds with increase in thickness of SnO$_2$ thin film from 30 to 120 nm. With further increase in thickness of SnO$_2$ sensing layer from 120 to 150 nm, the response time increases again from about 2 to 6 seconds (Fig.5.17). The variation of recovery time of SAW gas sensor with thickness of sensing thin film is also included in figure 5.17. The recovery time of SAW gas sensor was found to decrease from 565 to 45 seconds with increase in thickness of SnO$_2$ thin film from 30 to 120 nm. The recovery time of SAW sensor increases drastically to a much higher value of about 1800 s for higher thickness (150 nm) of sensing SnO$_2$ thin film (Fig.5.17). Since the recovery of 150 nm thin SnO$_2$ film based SAW gas sensor becomes very poor, 120 nm is considered to be the optimum thickness of sensing SnO$_2$ thin film for SAW sensor for detection of NO$_2$ gas. It can be concluded that SAW gas sensor having 120 nm thin SnO$_2$ film as sensitive coating exhibits the enhanced response \((-S_a \sim 30 \text{ MHz})\) for 20 ppm NO$_2$ gas with fast response and recovery time of about 2 and 45 seconds respectively.
Figure 5.16: Sensing response of SnO$_2$/SAW gas sensors towards 20 ppm NO$_2$ gas for SnO$_2$ sensing layer of thicknesses a) 30 nm, b) 60 nm, c) 90 nm, d) 120 nm, and e) 150 nm.
5.7.2 Effect of Sensing Layer Deposited at different Pressures

Since SAW gas sensor coated with 120 nm thin SnO\textsubscript{2} film is giving the best sensing response characteristics, the thickness of sensing layer was fixed and sputtering pressure for deposition of SnO\textsubscript{2} film was varied from 8 to 30 mT. The obtained response characteristics of SAW gas sensors having SnO\textsubscript{2} thin films grown at different sputtering pressures (8 to 30 mT) with exposure to 20 ppm NO\textsubscript{2} gas is shown in figure 5.18 (a) to (d). The SAW gas sensor having SnO\textsubscript{2} thin film grown at 30 mT sputtering pressure was found to exhibits a negative differential frequency shift (-S\textsub{a}) of about 13 MHz (Fig.5.18a). The sensing response (-S\textsub{a}) of SAW gas sensor increases (Fig.5.18b to d) significantly with coating of SnO\textsubscript{2} thin films grown at lower pressures (8 mT to 20 mT). It may be noted from figures 5.18 (b) to (d) that the shift in differential frequency (|S\textsub{a}|) of SnO\textsubscript{2}/SAW sensor decreases from 30.0 MHz to 25.0 MHz for SnO\textsubscript{2} thin film deposited with decrease in sputtering pressure from 20 mT to 8 mT.

The variation of response time and recovery time of the SnO\textsubscript{2}/SAW gas sensors is shown in figure 5.19 for sensing layer of SnO\textsubscript{2} deposited at different sputtering pressures. The response time of all prepared SAW sensors was found to be relatively small (2 to 6 s). The response time (6 s) of SAW gas sensor having SnO\textsubscript{2} thin film deposited at 8 mT was slightly higher (Fig.5.19), which decreases significantly (~ 2 s to 3 s) for sensing layers deposited at higher sputtering pressure (> 8 mT).

**Figure 5.17:** Variation of response time and recovery time of SAW gas sensors with the thickness of SnO\textsubscript{2} thin films for 20 ppm NO\textsubscript{2} gas
Figure 5.18: Sensing response ($-S_a$) of SAW gas sensors having SnO$_2$ thin films deposited at different sputtering pressures: a) 30 mT, b) 20 mT, c) 10 mT and d) 8 mT towards 20 ppm NO$_2$ gas
The plot of recovery time of SAW gas sensors as a function of sputtering pressure used for deposition of sensing layer is also shown in figure 5.19. The SAW sensors having SnO$_2$ thin film grown at moderate sputtering pressure (10 to 20 mT) was recovering fast (35 to 40 s) to the base line frequency value $[(\Delta f)_a = 0]$ after removal of target NO$_2$ gas. However the recovery time of SAW gas sensors coated with SnO$_2$ sensing layer at other sputtering pressure was found to be very large (> 370 s) and is attributed to the growth of SnO$_2$ thin film with very rough and porous microstructure (Fig.5.7). It can be identified from figure 5.19 that sensing SnO$_2$ thin film deposited at 10 mT sputtering pressure is advantageous for SAW sensor for detection of 20 ppm NO$_2$ gas because sensor exhibits a moderately high sensing response ($|-S_a| \approx 26.5$ MHz) with fast response time ($\sim 2$ s) and recovery time ($\sim 35$ s). Similarly the sensing layer grown at 20 mT gives enhanced sensing response ($|-S_a| \approx 30$ MHz) with relatively good response time ($\sim 2$ s) and recovery time ($\sim 45$ s).

![Graph](image)

**Figure 5.19:** Variation of response time and recovery time of SAW gas sensors for 20 ppm NO$_2$ gas as a function of the sputtering pressures (8 to 30 mT) for deposition of SnO$_2$ thin films

### 5.7.3. Effect of Concentration of NO$_2$ Gas and Cross Selectivity

The sensing response of the SAW gas sensor having sensing layer of SnO$_2$ deposited at 10 mT sputtering pressure was studied for varying concentration (10 to 20 ppm) of NO$_2$
gas and the observed variation is shown in figure 5.20. The SnO₂/SAW gas sensor gives the negative shift in differential frequency (response; |-Sₐ|) of about 25.0, 25.8 and 26.5 MHz with the exposure of NO₂ gas of 10, 15 and 20 ppm concentration respectively. The output of SAW gas sensor i.e. magnitude of differential frequency shift (|-Sₐ|) was found to increase linearly with increase in concentration of NO₂ gas (Fig.5.20). Therefore, SnO₂/SAW gas sensor prepared in present work using SnO₂ thin film grown at 10 mT, has the capability to detect NO₂ gas even at very low concentration.

![Graph showing variation of magnitude of differential frequency shift](image)

**Figure 5.20:** Variation of the magnitude of differential frequency shift of the SnO₂/SAW gas sensor as a function of the concentration of NO₂ gas

The SnO₂/SAW gas sensor was exposed to common interferant gases (CO₂, NH₃, H₂S, LPG, CH₄, and H₂) to study the cross sensitivity. The sensing response (|-Sₐ|) of the SnO₂/SAW gas sensor with exposure to various interferant gases is shown in figure 5.21. The concentrations of interferant gases H₂, CO₂, H₂S, NH₃, LPG, CH₄ were taken much higher and were 10,000, 5000, 1000, 1000, 10000, and 10000 ppm respectively for cross sensitivity study. The sensing response of SnO₂/SAW sensor obtained for 10 ppm of NO₂ target gas is also included in figure 5.21 for comparison. It may be noted from figure 5.21 that the prepared SnO₂/SAW gas sensor was showing negligible response (shift in differential frequency) with exposure to higher concentration (≥ 1000 ppm) of various
interferant vapors in comparison to that obtained for 20 ppm NO₂ gas. Among the various interferants tested in present study, the SnO₂/SAW gas sensor was giving maximum shift in differential frequency (-Sₐ~0.8 MHz) for 1000 ppm of H₂S gas molecules (Fig.5.21). However, the response was found to be negligibly small in comparison to that obtained for 10 ppm NO₂ target gas (|-Sₐ|=-26.5 MHz). Therefore SnO₂ thin film coated SAW gas sensor prepared in present work is capable of detecting NO₂ gas at low concentration level with enhanced response and negligible effect from the interferant gases.

Figure 5.21: Effect of various interferants on the sensing response of the SnO₂/SAW gas sensor

5.8 Sensing Mechanism of SnO₂/SAW Sensor for NO₂ Gas

It can be concluded from the above mentioned discussion that SnO₂ thin films coated SAW sensors are highly sensitive and selective for the detection of NO₂ gas. The centre frequency of SnO₂ coated SAW oscillators (f₀) are much less than the corresponding value of the uncoated SAW oscillator (f₀ = 433.8 MHz) by about (860 kHz to 39.35 MHz). After a small warm up time, when the surface of SAW sensor was not exposed to the target vapors, the value of difference frequency of dual SAW oscillator under the flow of inert carrier (N₂) gas is taken as the base line frequency [(Δf)₀ = f₀-f₁]. Upon exposure to target vapors, the shift in resonant frequency of SnO₂ coated SAW oscillator from f₀ to fₐ would cause a shift in difference frequency [Sₐ = (Δf)ₐ - (Δf)₀].
Therefore, the shift in differential frequency of $\text{SnO}_2$/SAW sensor, will be negative ($-S_a$) with increase in $f_1'$ from $f_1$ and positive ($+S_a$) with decrease in $f_1'$ from $f_1$. As already explained in detail in chapter 4, the three major contributions namely mass loading, acousto-electric interaction (electrical loading) and elastic loading are responsible for the sensing mechanism of a SAW gas sensor.

To understand the contribution of electrical loading towards the sensing mechanism of $\text{SnO}_2$ coated SAW sensor, independent measurements of electrical resistance of $\text{SnO}_2$ thin film were performed with exposure to NO$_2$ gas (as mentioned in chapter 4). The variation in resistance of 120 nm thin $\text{SnO}_2$ film deposited at 10 mT sputtering pressure on the surface of SAW resonator device with exposure of 20 ppm NO$_2$ gas is shown in figure 5.22. It may be noted from figure 5.22 that the resistance of the $\text{SnO}_2$ thin film increase slightly from 40.2 M$\Omega$ to 41.6 M$\Omega$ with exposure to NO$_2$ gas (20 ppm). The observed increase in resistance of n-type $\text{SnO}_2$ thin film with exposure to NO$_2$ gas is attributed to the fact that NO$_2$ gas is oxidizing in nature. The NO$_2$ molecules adsorbed at the Sn sites on the surface of $\text{SnO}_2$ thin film captures some free electron from the $\text{SnO}_2$. The reduction in concentration of electrons from conduction band of $\text{SnO}_2$ results in small increase in the resistance with interaction of NO$_2$ gas.

![Figure 5.22](image)

**Figure 5.22**: Change in the resistance of 120 nm thin $\text{SnO}_2$ thin film deposited at 10 mT on SAW resonator with the exposure to NO$_2$ gas (20 ppm)
The room temperature value of electrical resistivity of SnO\textsubscript{2} thin film was measured using Hall effect setup and found to be about $4.76 \times 10^5$ $\Omega$-cm. The measured value of the capacitance of the SnO\textsubscript{2}/SAW device is in few pF. Performing the similar analysis as done in chapter 4 for ZnO/SAW sensor (equation 4.15, chapter 4), it can be concluded that the contribution of acousto-electric interaction is not significant towards the observed sensing response of SnO\textsubscript{2}/SAW sensor for NO\textsubscript{2} gas. The non significant contribution of the acousto-electric interaction can further be justified by the resistance measurement of SnO\textsubscript{2} thin film as a function of time under exposure of NO\textsubscript{2} gas (Fig.5.22). It is important to note from figure 5.22 that the value of response time and recovery time for the change in the values of resistance of SnO\textsubscript{2} thin film under the exposure and removal of 20 ppm NO\textsubscript{2} gas is about 1.0 min. and 2.0 min. respectively. Whereas, the response time and recovery time of the SnO\textsubscript{2}/SAW sensor having SnO\textsubscript{2} sensing layer grown at 10 mT for 20 ppm NO\textsubscript{2} gas (Fig.5.19) was about 2 s and 35 s respectively, which are found to much lower than the corresponding values obtained from change in resistance measurement (Fig.5.22). The observed results confirmed that the acousto-electric interaction (electrical loading) is not playing a significant role in the sensing response of NO\textsubscript{2} gas by the prepared SAW sensor having SnO\textsubscript{2} thin film as sensing layer. Further the observed negative shift in differential frequency (response) for all prepared SAW sensor with exposure to NO\textsubscript{2} gas shows that mass loading is also not contributing significantly towards the sensing mechanism (already discussed in chapter 4 in detail). Therefore the change in the elasticity of the SnO\textsubscript{2} thin films with exposure to NO\textsubscript{2} gas is expected to be dominant sensing mechanism for SnO\textsubscript{2}/SAW sensor for NO\textsubscript{2} gas.

It may be recalled from figure 5.16 (a) to (d) that the response ($|S_a|$) of SnO\textsubscript{2}/SAW sensor towards 20 ppm NO\textsubscript{2} gas increases with increase in thickness of sensing SnO\textsubscript{2} thin film. However, the crystallite size of the sensing layer was also found to decrease continuously with increase in the thickness (Fig.5.4). Therefore, the correlation between the sensing response of SnO\textsubscript{2}/SAW gas sensor towards NO\textsubscript{2} gas was observed with the thickness of sensing SnO\textsubscript{2} layer.

The variation of the magnitude of negative differential frequency shift (response, $|S_a|$) of SnO\textsubscript{2}/SAW sensor towards 20 ppm NO\textsubscript{2} gas is plotted in figure 5.22 as a function of the crystallite size of sensing SnO\textsubscript{2} thin film.
The sensing response of SnO$_2$/SAW sensor was found to increase from 16 kHz to 16.6 MHz with decrease in crystallite size of sensing SnO$_2$ thin film from 15 nm to 12 nm, and thereafter saturates at a higher value of response $|-S_a| \approx 34$ MHz (Fig.5.23). The small size of the crystallites of the sensing SnO$_2$ layer seems to favour the contribution of the elastic loading with exposure to NO$_2$ gas (Fig.5.23) and hence giving higher magnitude of differential frequency shift ($|-S_a|$). With decrease in the crystallite size, the average porosity of the sensing thin films increases, and hence more and more target gas molecules will be able to adsorb on the surface of sensing SnO$_2$ thin film, resulting in an increase in the sensing response (magnitude of differential frequency shift). The response time and recovery time of SnO$_2$ SAW gas sensor initially decreases with increase in thickness of SnO$_2$ sensing layer up to 120 nm (Fig.5.17) and thereafter show an increase at higher thickness (> 120 nm). At small thickness (< 100 nm), the sensing film is non-uniform with rough microstructure and thereby giving higher value of increasing the response time and recovery time. A higher thickness of sensing layer (~ 120 nm), the film becomes uniform with dense and smooth microstructure, resulting in fast response time and recovery time of SnO$_2$/SAW gas sensors. However, at much higher thickness (> 120 nm) of SnO$_2$ thin film, the small crystallite size results in higher sensitivity along with poor response time and recovery time.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure5.23.png}
\caption{Variation of the magnitude of differential frequency shift of the SnO$_2$/SAW sensors as a function of crystallite size of sensing SnO$_2$ thin films}
\end{figure}
The magnitude of differential frequency shift (response) of SnO$_2$/SAW sensor was found to decrease with decrease in growth pressure of sensing SnO$_2$ layer from 20 to 8 mT (Fig.5.18) along with increase in response time and recovery time. The sensing SnO$_2$ thin film deposited at 30 mT and 8 mT (Fig.5.7) were very porous and rough along with large size crystallites. Therefore the elastic loading contribution is small thereby giving a relatively low sensing response. The small crystallite size of SnO$_2$ sensing layer grown at 10 mT and 20 mT was gives much higher response (negative shift in differential frequency) along with a fast response time and recovery time for SnO$_2$/SAW sensor towards 20 ppm NO$_2$ gas.

5.9 Conclusions

The SnO$_2$ thin films deposited under the varying pressure and of different thickness were studied for their structural, optical and electrical properties. The as-deposited SnO$_2$ thin films were polycrystalline with rutile structure. The SnO$_2$ thin films deposited under optimized condition exhibits fine microstructures with low surface roughness and uniformly distributed small size crystallites. The sensing films were highly transparent with optical transmission greater than 80 % in the visible region. The sensing response characteristics of SAW sensors having sensing SnO$_2$ thin films of varying thickness (30 to 150 nm) and deposited at different sputtering pressures (8-30 mT) have been studied for the detection of 20 ppm NO$_2$ gas. SAW sensors coated with 120 nm thin SnO$_2$ thin film exhibits enhanced sensitivity (\(|-S_a| \approx 26.5 \text{ MHz}\)) with fast response time (\(\sim 2 \text{ s}\)) and recovery time (\(\sim 35 \text{ s}\)) towards 20 ppm NO$_2$ gas. The sensing response of SnO$_2$/SAW sensor towards NO$_2$ gas is identified mainly due to elastic loading contribution, and the effect of mass loading and acousto-electric interaction is not significant. The change in elastic property of sensing SnO$_2$ thin film with exposure to NO$_2$ gas molecules was maximum for small crystallites, giving enhanced response for prepared SAW gas sensor. Influence of various interferant gases (ammonia, carbon dioxide, hydrogen sulphide, methane, hydrogen and liquefied petroleum gas was studied for SnO$_2$/SAW gas sensor and was very selective towards detection of NO$_2$ gas with enhanced response characteristics.