Chapter 4

Sensing Mechanism of the Distinct Response obtained for Liquor Ammonia

This chapter deals with the investigation on the various factors (mass loading, acousto-electric interaction and elastic changes) contributing the SAW gas sensing response. ZnO thin films are grown under different processing conditions (thickness, pressure and gas composition) to vary the surface morphology and structural property. The distinguished response obtained for the ZnO sensing layer based SAW device towards liquor ammonia is explained in detail as a function of processing condition and film thickness. Theoretical fitting is performed to evaluate the individual contribution from different factors affecting the gas sensing response. Attempt has been made to correlate the sensing response with the microstructural property of sensitive coating.
4.1 Introduction

ZnO thin film coated SAW sensor is found to be exhibiting distinct and enhanced response towards ammonia as compared to other vapors/gases (methanol, ethanol, acetone, benzene, xylene, N₂O and H₂) in the presence of water vapors. The response characteristics have been discussed in detail in chapter 3. In literature few work is reported related to the detection of ammonia utilizing different sensitive layers including polymers, metals, metal oxide thin films and nanocomposites [Shen et. al., 2005; D'Amico et. al., 1987; Jakubik et. al., 2006; Hsu et. al., 2009]. Few reports are also available in which the effect of humidity on sensing response of SAW gas sensor is investigated [Shen et. al., 2007; Shen et. al., 2004]. However in none of those reports, a change in the direction of sensing response i.e. both positive and negative shift in differential frequency (|S_a| and |-S_a|) for ammonia in the baseline of humidity have been reported as observed in the present work. However, Shen et. al., (2008) reported that with an increase in the ammonia concentration there is a corresponding decrease the negative frequency shift of SAW sensor, which is in accordance with the results obtained in the present work for ZnO film coated SAW sensor. It is to be noted that the response behaviour (both negative shift and positive shift) of ZnO coated SAW sensor on exposure to ammonia in the presence of humidity is peculiar. Hence, it is very important to identify the origin of sensing mechanism responsible for obtaining such peculiar behaviour. In the present chapter, an effort has been made to understand the origin of such response in the light of various factors affecting the SAW propagation characteristics and the properties of sensing layer.

4.2 Need to Understand the Sensing Mechanism

In literature, a lot of efforts have been made towards development of reliable SAW sensors for detection of a variety of toxic gases and vapors. Surprisingly systematic efforts towards the understanding of the origin of sensing mechanism of SAW gas sensors were very scarce due to its complex behaviour having influence from various factors. Since SAW sensors are very sensitive to the surface perturbations, the properties of the sensitive overlayer play a crucial role. Further it is to be noted that some target gases/vapors are sensitive to specific properties of the sensing layer including porosity, surface roughness, stress, electrical conductivity etc. In addition,
functional groups attached to the polymer chain and viscoelastic effects in case of polymer sensitive layer also play major role. To improve the sensor response characteristics, it is very important to understand the gas sensing mechanism since several factors are influencing the SAW sensor response such as change in mass, resistance, capacitance and elasticity of the sensitive thin film. Furthermore, in many cases more than one of these factors may influence the sensing response of SAW gas sensors simultaneously [Shen et. al., 2008]. In several reports, the decrease in frequency of SAW gas sensor on exposure to target analyte is attributed to the mass loading without any experimental or theoretical description [Korsah et. al., 1998; Lee et. al., 1998]. Few reports are available in which the change in resistance of sensitive layer was taken into consideration but the contribution of mass loading was not accounted [Jakubik et. al., 2007; Ippolito et. al., 2005]. SAW gas sensing mechanisms are also analyzed using some theoretical equations with custom made SAW fabrication [Anisimkin et. al., 1995a; Ghosh et. al., 2004; Anisimkin et. al., 2000]. Hence, there is an urgent need to understand the SAW sensing mechanism in detail and to find out the contribution of various factors towards the response characteristics of SAW gas sensors. This will led to the fabrication of novel SAW gas sensor structures for enhanced sensitivity and selectivity simultaneously. In the present chapter, an effort has been made to understand the sensing response of ZnO thin film coated SAW gas sensors towards liquor ammonia.

4.3 Factors Affecting the SAW Velocity/Frequency

All acoustic wave sensors are sensitive, to varying degrees, towards perturbations from various physical parameters. The range of phenomena that can be detected by acoustic wave devices can be greatly expanded by selecting suitable piezoelectric substrate (for superior acoustic propagation characteristics) coating the devices with desired sensitive materials that undergo changes in their mass, elasticity, or conductivity upon interaction with some physical or chemical stimulus. The acoustic sensors become mass, or gravimetric sensors, when the physical parameters (particles) are allowed to interact with the propagation medium (without any sensitive coating), changing the stress in the piezoelectric substrate. These sensors have the ability to detect pressure, torque, shock, and force under an applied stress that changes the dynamics of the propagating medium.
A wireless temperature sensor can be obtained by selecting the appropriate orientation of propagation in the piezoelectric substrate, along which the temperature coefficient of delay (TCD) is large. The propagating characteristics of medium changes with temperature, affecting the output frequency/velocity. However, vapor/gas sensors are realized when a coating of suitable material is applied on the surface of SAW device that absorbs only specific chemical vapors or gases. If the coating is sensitive to biological chemicals, the device becomes a biosensor. The change in the acoustic velocity in a SAW device depends on several factors including mass, stiffness, conductivity etc. [Ricco and Martin, 1991]. The net change in SAW velocity ($\Delta v$) can be obtained by adding the contribution of these factors, and can be written as [Ballantine et al., 1996]

$$\frac{\Delta v}{v_o} = \frac{1}{v_o} \left( \frac{\partial v}{\partial m} \Delta m + \frac{\partial v}{\partial c} \Delta c + \frac{\partial v}{\partial \varepsilon} \Delta \varepsilon + \frac{\partial v}{\partial \sigma} \Delta \sigma + \frac{\partial v}{\partial T} \Delta T + \frac{\partial v}{\partial p} \Delta p \ldots \right)$$

(4.1)

where $v_o$ is the phase velocity of SAW device, $\frac{1}{v_o} \left( \frac{\partial v}{\partial x} \Delta x \right)$ represents the change in velocity due to change in parameter $x$, $m$ is the mass adsorbed on sensitive coating, $c$ is the stiffness constant, $\epsilon$ is the dielectric constant, $\sigma$ is the surface electrical conductivity of sensitive layer, $T$ is the temperature and $p$ is the pressure.

The measured response of SAW gas sensor arises from the perturbations in the SAW propagation characteristics, specifically wave velocity and attenuation, resulting from interactions of target gas with sensitive surface layer. Surface acoustic waves propagating in a piezoelectric medium generate both mechanical deformation and an electrical potential, and therefore both mechanical and electrical couplings are present between the SAWs and sensing thin film.

Out of the several factors mentioned above (equation 4.1), three main factors that dominate the gas sensing response are mass loading, acousto-electric interaction (electrical loading) and elastic loading, since other parameters like temperature and pressure are kept constant (due to differential oscillator configuration) during sensing. The effects of these three factors on gas sensing response of SAW sensor are explained in the subsequent sections.
4.3.1 Mass Loading

Mass loading is the most utilized interaction in SAW gas sensor applications. If sensing layer on the surface of piezoelectric substrate is sufficiently thin or rigid, [Ballantine et. al., 1996]

1. it moves synchronously with the wave and
2. average kinetic density $U_k$ increases.

Change in average kinetic energy per unit area of the surface is [Ballantine et. al., 1996]

$$\Delta U_k = \frac{\Delta \rho_s}{4} \left( v_{x0}^2 + v_{y0}^2 + v_{z0}^2 \right) \quad (4.2)$$

where, $v_{x0}$, $v_{y0}$ and $v_{z0}$ are the SAW particle velocities along the x, y, and z cartesian coordinates and $\Delta \rho_s$ is the change in surface mass density. The particle velocities are related to particle displacement $U_i$, by $v_i = j\omega U_i$, where $\omega = 2\pi f_o$ is the angular frequency. The power density $P$ (power/area) carried by a wave can be related to wave energy $U$ (energy/volume) stored in a lossless medium as [Ballantine et. al., 1996]

$$P = U \nu \quad (4.3)$$

As in the lossless medium, $P$ is constant, differentiating equation 3 implicitly yields

$$\frac{\Delta \nu}{\nu_0} = - \frac{\Delta U}{U_0} \quad (4.4)$$

Thus increase in the kinetic energy results in the decrease in the wave velocity. Combining 4.2, 4.3 and 4.4 we have

$$\frac{\Delta \nu}{\nu_0} = - \frac{\omega \nu_0 \Delta \rho_s}{4} \left( \frac{v_{x0}^2}{\omega P} + \frac{v_{y0}^2}{\omega P} + \frac{v_{z0}^2}{\omega P} \right) \quad (4.5)$$

As almost all the wave energy is concentrated near the surface, surface particle velocities increase with operating frequency ($f_o$) in proportion to $(P_o)^2$. Thus, quantity in the parenthesis ($v_{io}^2/\omega P$), being independent of wave amplitude and depending only on the substrate material, remains constant for a fixed substrate. Taking all substrate-dependent constants together, the mass induced change in SAW propagation velocity can be written as [Ballantine et. al., 1996]
\[
\frac{\Delta v}{v_0} = -c_m f_0 \Delta \rho_s
\]  
(4.6)

where \(c_m\) is the mass sensitivity factor and is given by

\[
c_m = \frac{\pi v_0}{2} \left( \frac{v^{2}_{x0}}{\omega P} + \frac{v^{2}_{y0}}{\omega P} + \frac{v^{2}_{z0}}{\omega P} \right)
\]  
(4.7)

Therefore, the incremental change in center frequency of SAW sensor due to mass loading effect is given by equation 4.5 and rewritten as [Ballantine et. al., 1996]

\[
\frac{\Delta f}{f_0} = \frac{\Delta v}{v_0} = -\frac{\omega v_0 \Delta \rho_s}{4} \left( \frac{v^{2}_{x0}}{\omega P} + \frac{v^{2}_{y0}}{\omega P} + \frac{v^{2}_{z0}}{\omega P} \right) = -c_m f_0 \Delta \rho_s
\]  
(4.8)

### 4.3.2 Acousto-electric Interaction

SAW propagating in the piezoelectric medium generates a layer of bound charge on the surface which accompanies the mechanical wave. These bound charges are the source of the wave potential \(\Phi\) which generates an evanescent electric field \(E\), as shown in figure 4.1. When a conducting thin film is deposited onto the surface of piezoelectric substrate (SAW medium), charge carriers in the film redistribute to compensate the layer of bound charges generated by the propagation of surface wave [Ballantine et. al., 1996]. The effect of the interaction of acoustic wave with charge carriers on SAW propagation characteristics can be determined from an equivalent-circuit model that accounts for wave-generated conduction currents \(I_1\) in the deposited sensitive film and displacement currents \(I_2\) and \(I_3\) in the adjacent dielectric media [Ballantine et. al., 1996; Martin and Ricco, 1989], and the model is shown in figure 4.2. The time-varying surface charge generated by surface acoustic wave is represented by an alternating current source \((I_o e^{\text{int}})\). The current generated per unit area of surface, \(I_o\), is [Ballantine et. al., 1996].

\[
I_o = 2 K^2 \omega k^2 (\varepsilon_o + \varepsilon_s) P
\]  
(4.9)

where \(K^2\) is the electromechanical coupling coefficient, and \(\varepsilon_o\) and \(\varepsilon_s\) are the dielectric permittivities of air and substrate respectively, \(k\) and \(P\) are the acoustic wavenumber.
and power density (power per unit area) respectively. It may be noted from equation 4.9, that the current generated on the surface of SAW device is proportional to $K^2$ and $P$.

**Figure 4.1:** Evanescent electric field generated by a surface acoustic wave propagating along the surface of a piezoelectric substrate [Ballantine et. al., 1996].

**Figure 4.2:** Equivalent circuit model showing current flow in the sensing layer coated SAW sensor [Ballantine et. al., 1996]
Displacement currents are generated in the substrate ($i_3$) and air ($i_2$), due to the presence of the capacitances (per area of surface) of $k\varepsilon_s$ and $k\varepsilon_o$, respectively (Fig.4.2). Conduction current ($i_1$) in the sensitive overlayer is accounted by the shunt conductance $k\sigma_s$, where $\sigma_s$ is the sheet conductivity of the sensitive film. The sheet conductivity $\sigma_s$ of a film is related to the bulk conductivity $\sigma$, and film thickness $h$, by [Ballantine et. al., 1996]

$$\sigma_s = \sigma h \quad (4.10)$$

It is simple to derive the changes in velocity and attenuation arising from SAW/thin-film acousto-electric coupling. In the absence of a conducting thin film, energy is stored in the evanescent electric field generated by the acoustic wave. The complex power flow in this case (into the capacitors $k\varepsilon_s$ and $k\varepsilon_o$ in Fig.4.2) is [Ballantine et. al., 1996]

$$P_{T1} = \frac{i_0^2}{2|\omega k (\varepsilon_o + \varepsilon_s)|} \quad (4.11)$$

With a conducting thin film on the surface of SAW device, the power flow (in presence of acousto-electric interaction) becomes [Ballantine et. al., 1996]

$$P_{T2} = \frac{i_0^2}{2[\kappa^2\sigma_s + j\omega k (\varepsilon_o + \varepsilon_s)]} \quad (4.12)$$

The difference in power flows, i.e. due to acousto-electric effect is [Ballantine et. al., 1996].

$$P_T = P_{T2} - P_{T1} = -\frac{i_0^2}{2} \frac{\kappa^2\sigma_s}{|\omega k c_s (\kappa^2\sigma_s + j\omega k c_s)|} \quad (4.13)$$

where $c_s = \varepsilon_o + \varepsilon_s$ is the capacitance per unit length of the device. The change in SAW velocity ($\Delta v$) and attenuation ($\Delta\alpha$) can be related with the variation in power flow ($\Delta P_T$) due to acousto-electric effect as [Ballantine et. al., 1996]

$$\frac{\Delta\alpha}{k_o} - j \frac{\Delta v}{v_o} = \frac{\Delta P_T}{2k_o P} \quad (4.14)$$

where $v_o$ is the unperturbed SAW velocity and $k_o$ is the unperturbed acoustic wave number. Substituting $i_0$ from equation 4.9 into equation 4.13 gives the complex power
Typical variation of change in acousto-electric velocity ($\Delta v$) and attenuation ($\Delta \alpha$) are shown in figure 4.3 as a function of sheet conductivity ($\sigma_s$) of the sensitive thin film on the surface of piezoelectric quartz substrate having $K^2 = 0.11 \%$. The curves have the form of a relaxation response, SAW velocity decreases monotonically while attenuation goes through a peak with increase in sheet conductivity of sensing layer. The magnitude of the acousto-electric response is proportional to $K^2$ (equation 4.5 and 4.6), and is thus substrate dependent. Since $K^2$ is much larger for LiNbO$_3$ than for quartz (Table 1.2, Chapter 1), the acousto-electric interaction is expected to be more on the surface of LiNbO$_3$ based SAW devices. The peak in attenuation, as well as the maximum rate of decrease in velocity, occurs at a critical sheet conductivity defined by $\sigma_s = v_o c_s$.

![Figure 4.3: Variation of shift in acousto-electric velocity and attenuation as a function of the sheet conductivity of the sensitive thin film](image)
4.3.3 Elastic Changes

The effect of SAW induced deformations in sensitive overlayer having finite thickness and elastic properties are also important. Energy storage and power dissipation due to film deformation cause additional contributions to SAW velocity and attenuation. The mechanical properties of a linear, isotropic material can be specified by a bulk modulus, \( B \), and a shear modulus, \( G \) which are real-valued. The mechanical properties of ideal solid undergoing sinusoidal deformation, are best represented as complex quantities given by [Ferry, 1980].

\[
B = B' + jB'' \quad \text{and} \quad G = G' + jG''
\]  

(4.17)

The real parts of \( B \) and \( G \) represents the component of corresponding stress in-phase with strain, giving rise to energy storage in the film (consequently \( B' \) and \( G' \) are referred as storage moduli). The imaginary parts represent the component of stress \( 90^\circ \) out of phase with strain, giving rise to power dissipation in the film (thus, \( B'' \) and \( G'' \) are called loss moduli). The wave energy stored and dissipated in film depends on strain modes generated by the SAW [Ballantine, 1996]. Two distinct regimes of film behaviour are:

1. Entire film moves synchronously with the substrate surface, resulting in uniform displacement across the film thickness (acoustically thin film).
2. Entire film does not move synchronously with the substrate, and a lag between the upper and lower part of the film exist (acoustically thick film).

Figure 4.4 shows the deformation arising in an acoustically thin and thick film by SAW. Displacements \( u_i \) are constant across the film thickness, and only gradients in the plane of the film arise in acoustically thin film (Fig4.4a). In figure 4.4, the gradient in \( u_r \) leads to regions of compression and tension in the film, while gradient in \( u_y \) gives bending. The regime of film can be determined from the ratio \( R \) of cross-film to in-plane gradients induced by SAW [Martin et. al., 1994]

\[
R = \frac{Afv_{\alpha \phi}}{|G|}
\]  

(4.18)

where \( \rho \), \( h \), and \( G \) are the film density, thickness, and shear modulus respectively and \( A \) is a substrate dependent parameter. When the film is sufficiently thin (small \( h \)) and rigid
(large \( G \)), such that \( R \ll 1 \), in-plane gradients dominate over surface-normal gradients and the film is acoustically thin. When film properties are such that \( R \geq 1 \), inertial lag becomes significant so that surface-normal gradients are dominant (Fig.4.4b), and the film is acoustically thick.

If the film is acoustically thin \((R \ll 1)\), then displacements are constant across the film thickness, and only gradients in the plane of the film arise. The SAW induced film deformation can be decomposed into three translations \((\text{in } x, y, \text{ and } z\text{-directions})\) and three strain modes (Fig.4.4). An important parameter in determining the contribution of each strain mode in perturbing SAW propagation is the modulus \( E^i \), the ratio of stress to strain associated with each strain mode. The values of \( E^i \) is listed in Table 4.1 in terms of the intrinsic elastic properties of the film, represented in terms of the Lame constants \((\lambda', \mu)\) and the bulk and shear moduli \((B, G)\) [Ballantine, 1996].

**Table 4.1: Moduli Associated with the Strain Modes generated by a SAW in an acoustically thin film \((R \ll 1)\) [Martin et. al., 1994]**

<table>
<thead>
<tr>
<th>Strain Mode</th>
<th>Displacement Gradient</th>
<th>Modulus Definition</th>
<th>Molulus ( E^i )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \partial u_i / \partial z )</td>
<td>( E^{(1)} = T_{1i}/(2S_{1i}) )</td>
<td>( \mu ) ( G )</td>
</tr>
<tr>
<td>Transverse Sheer</td>
<td>( \partial u_i / \partial z )</td>
<td>( E^{(2)} = T_{2i}/(2S_{2i}) )</td>
<td>( \approx 0 ) ( \approx 0 )</td>
</tr>
<tr>
<td>Bending</td>
<td>( \partial u_i / \partial z )</td>
<td>( E^{(3)} = T_{3i}/(S_{3i}) )</td>
<td>( 4\mu(\lambda' + \mu) ) ( \lambda'/2\mu ) ( 4G(3B + G) ) ( 3B + 4G )</td>
</tr>
<tr>
<td>Longitudinal Compression</td>
<td>( \partial u_i / \partial z )</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

For acoustically thin films, the impedance associated with each film translation is \( j\omega \rho h \), and with each strain mode is \( -(j\omega h E_i)/V_o^2 \), where \( E^i \) are taken from Table 4.1 [Martin et. al., 1994]. Thus, from a perturbation analysis, the change in SAW propagation arising from acoustically thin films is [Martin et. al., 1994]

\[
\frac{\Delta \alpha}{k_o} - j \frac{\Delta v}{v_o} = j\omega h \left( \sum_{i=1}^{3} c_i \left( \rho - \frac{E^{(i)}}{v_o^2} \right) \right) \tag{4.19}
\]

where the SAW-film coupling parameter \( c_i = v_{io}^2/(4k_o P) \); \( v_{io} \) denotes the surface particle velocity (related to surface displacement \( u_{io} \) by \( v_{io} = j\omega u_{io} \)) in each direction, and \( P \) is the SAW power density.
Figure 4.4: Deformation generated by a SAW (a) in an acoustically thin \((R \ll 1)\) film, in which in-plane displacement gradients (due to sinusoidal wave variation) dominate, and (b) in an acoustically thick \((R \geq 1)\) film, where cross-film gradients (due to inertial film lag) also arise [Ballantine, 1996].

Equating real and imaginary parts of equation 4.19, yields the change in velocity and attenuation due to interaction of SAW with film. The intrinsic elastic moduli are real for elastic film, resulting in \(\Delta \omega/\omega_0 = 0\). Substituting the \(E_i\) in terms of the Lame constants \((\lambda', \mu)\) from Table 4.1 for into an acoustically thin \((R \ll 1)\), elastic \((B'' = G'' = 0)\) film into Tiersten formula [Tiersten and Sinha, 1978], we have
where \( C_e \) is the elastic sensitivity factor.

### 4.4 Sensing Mechanism of Liquor Ammonia by ZnO/SAW Sensor

The observed sensing responses of ZnO/SAW gas sensor towards liquor ammonia (chapter 3) has been analyzed in the light of mass loading, acousto-electric interaction and elastic effect and are discussed in the following sections.

The centre frequency of ZnO thin film coated SAW oscillators (\( f_i \)) are less than the corresponding frequency of the uncoated (reference) SAW oscillator (\( f_0 = 433.8 \, \text{MHz} \)) by few MHz. After a small warm up time, and under the flow of inert carrier gas (N\(_2\)), the value of difference frequency (\( \Delta f = f_0 - f_i \)) of the dual oscillator is taken as baseline frequency. The schematic of the frequencies of reference SAW oscillator (\( f_0 \)), coated SAW oscillator (\( f_i \)), difference frequency of SAW sensor (\( \Delta f \)) in dual oscillator mode and shift in differential frequency (\( \pm S_a \)) in the absence and presence of target analyte is shown in figure 4.5. Upon exposure to target gas, the change in the centre frequency of ZnO coated SAW oscillator (from \( f_i \) to \( f_i' \)) cause a change in difference frequency of dual oscillator from \( \Delta f_a = f_0 - f_i \) to \( \Delta f_g = f_0 - f_i' \) where \( \Delta f_a \) is the frequency of dual oscillator under flow of carrier N\(_2\) gas without any analyte, and \( \Delta f_g \) is the difference frequency of dual oscillator with exposure to target gas. Therefore, the shift in differential frequency \( +S_a = \Delta f_g - \Delta f_a \) will be negative, if the frequency of coated SAW device increases (\( f_i \) to \( f_i' \)) with the interaction of analyte (Fig.4.5c). Since baseline frequency (\( \Delta f_a = f_0 - f_i \)) in the present work is in MHz and the observed shifts in the frequency of coated SAW oscillator (\( f_i \) to \( f_i' \)) due to interaction with target vapors are in kHz i.e. \( |f_0 - f_i| > |f_0 - f_i'| \) or \( \Delta f_a > \Delta f_g \), the zero cross over related sign changes in differential frequency (\( \Delta f \)) will not occur due to shift in \( f_i' \) from \( f_i \) under exposure of analyte. Therefore the baseline of the SAW gas sensor in dual oscillator mode has been offset to zero frequency i.e. \( (\Delta f_a = f_0 - f_i = 0) \) for convenience during sensing measurement.
Figure 4.6: The variation in differential frequency with sensor frequency

(a) Centre frequency of coated device decrease from $f_0$ to $f_s$

(b) If $f_s$ decreases with interaction of analyte

(c) If $f_s$ increases with interaction of analyte
Various parameters are expected to contribute to the response characteristics of SAW gas sensor such as mass loading, electric loading, elastic loading, temperature, pressure etc. While studying the response characteristics in the present case, pressure was kept constant on the surface by maintaining a constant flow of target vapors. The effect of small change in ambient temperature on the sensing response of SAW sensor is minimized by measuring the shift in differential frequency under dual SAW oscillator configuration. Hence mass loading, electric loading (acousto-electric interaction), and elastic loading are the main perturbation effects which are expected to contribute to the observed sensing response characteristics of SAW gas sensor. The contribution of mass loading on the surface of SAW device results in a decrease in the velocity (equation 4.8) and hence frequency ($f_i$ to $f_i'$) decreases, so the shift in differential frequency ($+S_a$) will be positive (Fig.4.5b). Similarly with increase in elasticity of the sensing layer (equation 4.20), frequency increases ($f_i$ to $f_i'$) and hence the shift in differential frequency ($-S_a$) should be negative (Fig.4.5c). However the effect of elastic loading results in both positive or negative shift ($\pm S_a$) depending on the variation in $\sigma_s$ of sensing layer with target gas.

To study the origin of sensing mechanism of the observed distinct response of ZnO/SAW sensors, the saturation response was taken for different thickness of ZnO sensing layer on exposure to headspace vapors of liquor ammonia (25%) for long duration (2 mins.) (as described in chapter 3) and is shown in figure 4.6.

**Figure 4.6:** Saturated response of ZnO/SAW sensors having different thickness (20 to 80 nm) of sensing ZnO layer on exposure to headspace vapors of liquor ammonia (25%)
As already shown in chapter 3, 40 nm thin ZnO film coated SAW sensor was most sensitive to liquor ammonia vapors (Fig. 4.6). Furthermore, highly selective response characteristics towards liquor ammonia, exhibiting initially a negative shift in differential frequency \((-S_a)\) followed by a positive shift in differential frequency \((+S_a)\) was observed.

4.4.1 Contribution of Acousto-electric Interaction

The effect of acousto-electric interaction (electrical loading) on the SAW velocity and hence frequency of the SAW device is

$$\Delta V = -\frac{K^2}{2} \times \Delta \left( \frac{1}{1 + \left( \frac{V_o C_s}{\sigma_s} \right)^2} \right)$$ (4.15)

The interaction of target gas with sensing layer results in the change in carrier concentration and thereby gives the variation in saw velocity due to acousto-electric interaction. To understand the contribution of electrical loading on the observed sensing response of SAW gas sensors (chapter 3), independent measurements on the resistance and capacitance of the 40 nm thin ZnO sensitive coating was performed in the presence and absence of liquor ammonia (25%). Thickness of ZnO layer was chosen to be 40 nm thin because SAW sensor having 40 nm thin ZnO film exhibit the maximum response (Fig. 4.6). Since the device used in the present work is one port SAW resonator, having single IDT, contact pads of the IDT were utilized for resistance measurement of the sensitive coating of ZnO. The schematic of the experimental set up used for the resistance measurement is shown in figure 4.7.

Figure 4.7: Schematic of the experimental set up for the measurement of electrical resistance of ZnO thin film (40 nm) deposited on SAW device.
Initial resistance of the as grown ZnO thin film was found to be about 5 GΩ, therefore a resistance (10.2 MΩ) was connected in parallel for transient measurement of resistance with exposure to liquor ammonia vapors. The net resistance was measured using a digital multimeter (Protek 506) interfaced with PC for real time data acquisition. The multimeter refreshes the value of resistance periodically with in a time interval of 1.0 second.

The observed change in resistance in the parallel combination with long exposure (~2 min.) to vapors of liquor ammonia with sensing ZnO thin film is shown in figure 4.8. A decrease in the net resistance of parallel combination from 10.2 to 8.2 MΩ was obtained corresponding to a decrease in resistance of the ZnO thin film from 5 GΩ to about 45 MΩ. It is interesting to observe from figure 4.8 that the ZnO thin film (coated over SAW resonator device) recovers the initial stable resistance value (5 GΩ) very rapidly when the liquor ammonia vapors are removed. The value of rise time and fall time for the change in resistance of ZnO thin film is about 42 seconds and 5 seconds respectively (Fig.4.8).

![Figure 4.8](image-url)

**Figure 4.8:** Change in net resistance of the parallel combination of ZnO thin film with 10.2 MΩ resistance with exposure to vapors of liquor ammonia for 2 minutes
The fractional change in the frequency or SAW velocity due to acousto-electric interaction effect is related to the change in conductivity and capacitance per unit length of ZnO sensing film (equation 4.15). The electrical conductivity of ZnO thin film was measured independently using Hall effect studies. The values of resistivity, mobility and carrier concentration of ZnO thin film was about $1.5 \times 10^3 \, \Omega \cdot \text{cm}$, $9.6 \, \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ and $1.4 \times 10^{15} \, \text{cm}^{-3}$ respectively. The capacitance of the ZnO thin film (40 nm) was measured by using a LCR meter (Agilent 4284A) in the same configuration in which resistance was measured. The variation of capacitance of ZnO thin film as a function of frequency over the range 20 Hz to 1.0 MHz is shown in figure 4.9. The capacitance of ZnO thin film was found to exhibit small frequency dispersion (Fig.4.9). The value of capacitance shows a decrease from 0.80 to 0.49 pF with increase in measured frequency from 20 Hz to 100 kHz and found to saturate at a value of about 0.48 pF (Fig.4.9) at higher frequencies (>100 kHz).

![Figure 4.9: Variation in the capacitance of ZnO thin film as a function of frequency](image)

It is important to emphasize that the value of capacitance of ZnO thin film in the measured frequency region is in picofarads and the observed decrease in its value is very small (Fig.4.9) in high frequency region (≥100 kHz). Further on exposure to vapors of liquor ammonia to the surface of ZnO coated SAW resonator, no significant change in the capacitance of the sensing layer was observed and the capacitance of ZnO layer was still in picofarads. Substituting the obtained values of conductivity and
capacitance of sensing ZnO thin film in equation 4.15, it is found that the factor $(C_s V_o / \sigma_s)^2 << 1$. Since the conductance of ZnO thin film increases by about two orders of magnitude (Fig.4.8) and the change in capacitance is insignificant after exposure to vapors of liquor ammonia, so the condition $(C_s V_o / \sigma_s)^2 << 1$ is still valid. Therefore from equation 4.15, we can identify that the acousto-electric interaction is not playing a significant role in the observed sensing response characteristic of ZnO thin film based SAW gas sensor for liquor ammonia vapors. It is to be noted from equation 4.15 that acousto-electric interaction towards sensing response of SAW sensor is significant only if $(C_s V_o \geq \sigma_s)$, which is not feasible in the present study. Further low value of electromechanical coupling coefficient $(K^2)$ of quartz (of SAW resonator) is also responsible for negligible contribution of acousto-electric effect. Hence the possible contributions to the observed sensing response of ZnO/SAW sensor towards liquor ammonia are expected from the mass loading and elastic loading only.

4.4.2 Mass Loading and Elastic Loading Contributions

Mass loading and elastic loading are expected to change the sign of shift in differential frequency ($S_a$) of SAW sensor. Mass loading of target vapors (liquor ammonia) on the surface of ZnO/SAW sensor reduces the velocity of propagating SAW (equation 4.8), resulting in a decrease in resonant frequency from $f_s$ to $f_s'$. The decrease in resonant frequency gives a positive shift in the differential frequency (+$S_a$) due to mass loading effect. Since acousto-electric contribution towards the SAW sensing response is insignificant, the observed negative shift in differential frequency (-$S_a$) is expected to be due to elastic loading contribution only. The interaction of target vapors with the surface of SAW sensor is expected either to stiffening (increase in elasticity) or softening (decrease in elasticity) of the sensing layer. Therefore the centre frequency of ZnO/SAW oscillator ($f_o'$) may either increase or decrease due to elastic effect. The observed negative shift in the differential frequency ($S_a$) in the initial part of the sensing response of SAW sensor towards liquor ammonia (Fig.4.6) cannot be attributed to either mass loading effect (as it led to positive shift only) or acousto-electric interaction (which is insignificant in the present case), and is expected to be due to the elastic loading effect only. Therefore based on the obtained results, it is apparent that the contribution of elastic loading towards sensing response of liquor ammonia is dominating initially giving rise to negative differential frequency shift ($S_a$). On the other
hand, mass loading effects become dominant in the later part of the SAW sensing response giving rise to \((+S_a)\). The mass loading and elastic loading when acting simultaneously will change the SAW velocity and hence resonant frequency \((f_s, f_s')\) of the coated SAW oscillator as (equations 4.6 and 4.20)

\[
\frac{\Delta V}{V_0} = \frac{f_s' - f_s}{f_o} = -C_m f_o \Delta(\rho_s) + C_e f_o h \Delta \left( \frac{4 \mu}{V_o^2} \right) \times \left( \frac{\mu + \lambda'}{\mu + 2\lambda'} \right)
\]

(4.21)

where \(f_s', f_s\) is the change in frequency of a single ZnO coated SAW (ZnO/SAW) oscillator due to surface perturbations during interaction of target vapors with SAW sensor, \(f_o\) is the unperturbed frequency of bare SAW reference oscillator, \(\mu\) and \(\lambda'\) are the Lame's constants, \(C_m\) and \(C_e\) are the sensitivity coefficients of mass and elasticity respectively, \(h\) is the thickness of the ZnO sensing thin film and \(\rho_s\) is the surface density (mass per unit area) of the sensing thin film. It is reported that \(\lambda'\) and \(\mu\) can be expressed in terms of young’s modulus (E) and Poisson’s ratio (v) as [Hietala et. al., 2001]

\[
\mu = \frac{E}{2(1+v)} \quad \text{and} \quad \lambda' = \frac{E}{3(1-2v)}
\]

(4.22)

After substituting the values of \(\mu\) and \(\lambda'\) from equation 4.22, the equation 4.21 can be rewritten as;

\[
\frac{\Delta V}{V_0} = \frac{f_s' - f_s}{f_o} = -C_m f_o \Delta(\rho_s) + C_e f_o h \Delta \left( \frac{1}{V_o^2} \right) E \times \left( \frac{4v-5}{5v^2+v-4} \right)
\]

(4.23)

The reported value of ‘v’ for ZnO is in the range 0.22 to 0.35 [Internet 15]. The corresponding value of term \(\left( \frac{4v-5}{5v^2+v-4} \right)\) in equation 4.23 is found to vary from 1.16 to 1.18 for the ZnO thin film, and can be assumed constant as the change in value of this term is insignificant. The equation 4.23 becomes

\[
\frac{\Delta V}{V_0} = \frac{f_s' - f_s}{f_o} = -C_m f_o \Delta(\rho_s) + C_e f_o h \left( \frac{1}{V_o^2} \right) \left( \frac{4v-5}{5v^2+v-4} \right) \cdot (\Delta E)
\]

(4.24)

Equation (4.24) can be simplified and written as

\[
\text{Shift in frequency, } (f_s' - f_s) = -p\Delta m + q\Delta E
\]

(4.25)
where \( p \) and \( q \) are constants given by
\[
q = C_{(g)} f_0^2 \frac{1}{\nu_0^2} \left( \frac{4v-5}{5v^2 + v - 4} \right)
\]
and
\[
p = \frac{C_m f_0^2}{A}
\]
where \( \Delta m \) is the change in mass on the surface of coated SAW oscillator, \( \Delta E \) is the change in Young's modulus and \( A \) is surface area of sensing layer. Since frequency of the reference (uncoated) SAW oscillator \((f_0)\) does not show any significant frequency shift due to the exposure of target vapors, and base line frequency \([(\Delta f)_a = f_o - f_s]\) of differential oscillator has been offset to zero, the shift in differential frequency \([S_a = (\Delta f)_g - (\Delta f)_a \approx -(f_s' - f_s)]\) is related to change in frequency of coated SAW oscillator alone with the exposure of target (liquor ammonia) vapor, and the sign of \( S_a \) will depend on the condition \( f_s' < f_s \) (giving \((+S_a)\) or \( f_s' > f_s \) (giving \((-S_a)\)) for \( f_s < f_o \) (Fig.4.5). For ZnO/SAW sensor in differential mode configuration, the condition is \( f_s' < f_s \) and \( f_s < f_o \) therefore the response (shift in differential frequency) becomes
\[
S_a = (\Delta f)_g - (\Delta f)_a = p\Delta m - q\Delta E
\]  

4.4.3 Theoretical Fitting of Sensing Response Curve

Direct and precise way of separating the contribution of mass loading and elastic loading from the output sensing response of a single IDT SAW structure is difficult. Harding et. al., (1997) used an exponential equation which fitted well with the sensing response of SAW sensor arising due to mass loading. The kinetics of mass loading at a fixed analyte concentration on the surface of SAW sensor can be expressed as [Harding et. al., 1997]

\[
\frac{dm}{dt} \propto (m - m_o)
\]  

where \( m_o \) is the maximum mass that can be adsorbed on the surface of sensing thin film deposited on the surface of SAW device and \( m \) is the mass adsorbed at any instant of time \( t \) with boundary conditions \( m = 0 \) at \( t = 0 \), and \( m = m_o \) at \( t = \infty \). The solution of equation 4.27 becomes
\[
\Delta m = m_o(1 - e^{-bt})
\]  
4-21
where $\Delta m$ is the change in mass adsorbed on the surface of sensing layer between $t = 0$ to $t$, and $b$ is a constant. Since the form of mass loading and elastic loading terms in equation 4.26 are similar, the elastic loading term can also be represented as

$$\Delta E = E_o (1 - e^{-dt})$$  \hspace{1cm} (4.29)

where $E_o$ is the maximum young modulus of sensitive coating with adsorption of target gas at $t = \infty$, and $d$ is constant. Therefore variation in the shift in differential frequency $(S_a)$ of SAW gas sensor due to the contribution from both the mass loading and elastic loading on adsorption of target (liquor ammonia) vapors on the surface of sensing layer can be expressed as a sum of two exponential functions given by equations 4.28 and 4.29 respectively, and the response (equation 4.26) will be

$$S_a = (\Delta f)_g - (\Delta f)_a = a (1 - e^{-bt}) - c (1 - e^{-dt})$$  \hspace{1cm} (4.30)

where $a = pm_o$ and $c = qE_o$ are the constants. By simultaneously fitting the experimentally obtained sensing response curves using equations 4.28 and 4.29, the specific contribution of mass loading and elastic loading towards response can be obtained.

### 4.5 Effect of Thickness of Sensitive Coating

The observed sensing response of SAW gas sensors for varying thickness (20 to 80 nm) of ZnO sensing layer (Fig.4.6) were chosen to identify the contributions from various factors. As discussed earlier the contribution of acousto-electric interaction towards observed sensing response of ZnO/SAW sensor in the present work is negligible. The experimental sensing response curves of figure 4.6 were fitted using equation 4.30 with $a$, $b$, $c$ and $d$ as the fitting parameters. The best fitted theoretical curves are shown in figures 4.10 a, b and c respectively for different thickness (20, 40 and 80 nm) of sensing ZnO thin film. The sensing response is found to have the contribution from both mass loading and elastic loading. The small deviations observed between the measured sensing response data and the best fitted response curves (Fig.4.10a to c) are due to the fact that the vapor adsorption on the surface of sensing layer is a dynamic phenomenon where various factors may affect the frequency shifts though their contribution is small.
Figure 4.10: Best fitting of the measured response data towards liquor ammonia for ZnO sensing films of different thickness: a) 20 nm b) 40 nm and c) 80 nm. The individual contribution of mass loading and elastic loading towards sensing response are also shown.
It may be noted from figure 4.10 (a) to (c) that the contribution of mass loading towards the frequency shift of the SAW gas sensor for all thickness of ZnO sensing layer is positive, whereas the contribution of elastic loading in the present study is towards the negative shift in differential frequency. The sensing response of ZnO/SAW sensors i.e.
net shift in differential frequency could be positive or negative (Fig.4.10) depending upon the dominating contribution from either mass loading or elastic loading. The contribution of both mass loading and elastic loading towards the sensing response was found to increase initially with increase in time and thereafter tends to saturate at a constant value (Fig.4.10). The observed increase in the contribution of both parameters (mass loading and elastic loading) with time is due to increase in the adsorption of target vapor (liquor ammonia) molecules on the surface of ZnO sensing layer, and a saturated contribution was achieved when maximum number of molecules get adsorbed on the surface of ZnO/SAW sensor after a sufficient amount of time. The contribution due to elastic loading is dominating during the initial phase of liquor ammonia interaction (left side of dotted lines in Fig.4.10 (a) to (d)) for all thickness (20 to 80 nm) of ZnO sensing layer, and therefore the sensing response (Fig.4.6) of ZnO/SAW gas sensor initially exhibit a negative shift in differential frequency (-S_a). The mass loading contribution dominates during the later part (right side of dotted lines in Figs.4.10 (a) to (d)) of the interaction of liquor ammonia with ZnO/SAW sensor. Furthermore, the saturated contribution of mass loading was found to be much higher in comparison to the saturated contribution of elastic loading (Fig.4.10) for all prepared ZnO/SAW sensors hence the sensing response (Fig.4.6) is showing a positive shift in differential frequency (+S_a) after interaction with liquor ammonia with some delay. The contribution of mass loading and elastic loading towards the sensing response of ZnO/SAW gas sensor is strongly dependent on the thickness of sensing ZnO layer. The variation of the individual contribution of mass loading and elastic loading towards sensing response (shift in differential frequency) obtained for different thickness of ZnO sensing layer are shown in figures 4.11 (a) and (b) respectively as a function of time of the interaction of liquor ammonia with SAW gas sensors. The saturated value of positive shift in differential frequency (+S_m) of ZnO/SAW sensor due to only mass loading contribution for 20, 40 and 80 nm thin ZnO sensing films are found to be 720, 907 and 710 kHz respectively (Fig.4.11a). Hence the contribution of mass loading towards sensing response of ZnO/SAW sensor increases with increase in thickness of sensing layer from 20 to 40 nm and decreases with further increase in thickness to 80
nm. The observed behaviour is attributed to the increase number of absorption sites for target vapor with increase in thickness of sensing ZnO layer from 20 to 40 nm, due to which contribution of mass loading increases. As discussed in chapter 1, the energy of the surface acoustic waves is concentrated more near the surface. If the thickness of ZnO over layer on the surface of SAW resonator is higher (~80 nm), there will be a significant change in the distribution of SAW energy on its upper surface and the lower surface. Although, the number of target analyte adsorbed on 80 nm thin ZnO film might be more, but overall effect will lead to decrease in the SAW velocity (resonant frequency) and hence a reduced value of differential frequency shift has been obtained. The shifts in differential frequency (response) due to elastic loading effect alone are negative ($-S_e$) for all prepared ZnO/SAW sensors having a saturated contribution of 296, 394 and 414 kHz for 20, 40 and 80 nm thin ZnO film respectively. In the case of elastic loading, the sensing response (magnitude of negative shift in differential frequency) keeps on increasing with ZnO sensing layer thickness. With increase in the thickness of ZnO film, crystallite size increases (chapter 3) and the change in microstructure may be favorable for the observed increase in the elastic contribution and hence resulting in the more negative shift in the differential frequency. The response time and recovery time of ZnO/SAW sensor along with the microstructural parameters (stress, crystallite size, roughness) of the ZnO thin films of different thickness are presented in table 4.2. As can be seen from table 4.2, the response time of the SAW sensor having 40 nm ZnO thin chemical interface is minimum, whereas increases both with increase and decrease of ZnO film thickness.

Table 4.2: The values of $+\Delta f$, $-\Delta f$, response time, recovery time along with the physical parameters (thickness, stress, crystallite size and roughness) of ZnO thin films

<table>
<thead>
<tr>
<th>Thickness (nm)</th>
<th>Stress $x10^{10}$ (dynes/cm$^2$)</th>
<th>Crystallite size (nm)</th>
<th>Roughness (nm)</th>
<th>Mass loading $+\Delta f$ (kHz)</th>
<th>Elastic loading $-\Delta f$ (kHz)</th>
<th>Response time (s)</th>
<th>Full Recovery time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>5.5</td>
<td>12</td>
<td>10</td>
<td>720</td>
<td>296</td>
<td>28</td>
<td>45</td>
</tr>
<tr>
<td>40</td>
<td>2.9</td>
<td>17</td>
<td>4</td>
<td>907</td>
<td>394</td>
<td>21</td>
<td>180</td>
</tr>
<tr>
<td>80</td>
<td>1.5</td>
<td>20</td>
<td>2.5</td>
<td>710</td>
<td>414</td>
<td>23</td>
<td>680</td>
</tr>
</tbody>
</table>

4-26
ZnO thin films having different surface morphology also differs in their thickness and hence multiple effects are playing crucial role. The obtained results indicate that the physical properties and microstructure of the sensing layer may govern the response characteristics of ZnO/SAW gas sensor to a great extent. Therefore in order to identify the correlation between the properties of sensing layer with the sensing response characteristics for liquor ammonia, ZnO thin films were deposited under varying growth conditions (growth pressure and oxygen to argon ratio in reactive gas) and SAW response characteristics were studied in detail towards liquor ammonia in the subsequent sections.

4.6 Effect of Processing Pressure

ZnO thin films were deposited under varying sputtering pressure from 10 to 40 mT while keeping all other processing conditions same as presented in Table 3.3 in chapter 3. The thickness of the ZnO sensing film was maintained constant at 40 nm that resulted in maximum SAW response towards liquor ammonia in comparison to other thickness (Fig.4.6). ZnO thin films were deposited on both ST-X quartz substrates and SAW resonators simultaneously. For characterization of ZnO thin films ST-X quartz substrate was deliberately chosen since the SAW resonator is fabricated on the same piezoelectric substrate only.

4.6.1 Structural Characterization of ZnO Thin Films

XRD pattern of ZnO thin films deposited on ST-X quartz substrate at different sputtering pressures is shown in figure 4.12. The XRD pattern of all as-grown thin films shows only reflection corresponding to (002) plane of wurtzite structure of ZnO, indicating growth of preferred oriented ZnO thin films with c-axis normal to the surface of quartz substrate. The surface free energy of (002) plane in wurtzite ZnO structure is minimum as compared to other planes [Menon et. al., 2008]. Therefore the growth of a preferred c-axis oriented ZnO thin film was observed even at room temperature substrate in the present study. The (002) XRD peak for all ZnO thin films grown under varying growth pressure was observed at Bragg’s angle (20) which is much lower than
the corresponding reported value (34.42°) for bulk ZnO [Menon et. al., 2008]. The deviation in the 2θ value is due to the presence of stress in the deposited ZnO thin films [Menon et. al., 2008]. The position of (002) reflection peak of ZnO film was found to depend strongly on the sputtering pressure. The deviation in the position of (002) XRD peak from the corresponding bulk value was found to be minimum for the films grown at 20 mT sputtering pressure, and increases on either side with an increase or decrease in the sputtering pressure.

![XRD pattern of ZnO thin films deposited at different sputtering pressures](image)

**Figure 4.12: XRD pattern of ZnO thin films deposited at different sputtering pressures**

The variation of lattice constant (c) of ZnO thin film as a function of sputtering pressure is shown in figure 4.13. The estimated value of lattice constant 'c' for all deposited ZnO films are found to be well in the range reported for ZnO thin films by other workers [Menon et. al., 2008; Gupta and Mansingh, 1996]. The lattice constant (5.27 Å) of ZnO thin film grown at higher pressure (40 mT) was much higher than the corresponding bulk value (5.22 Å) indicating that the unit cell is elongated along the c-axis. The lattice constant starts decreasing with decrease in growth pressure and approaches the bulk value for ZnO thin film deposited at 20 mT (c ≈ 5.239 Å). However, the lattice constant again shows an increase when growth pressure (10 mT) was reduced further (Fig.4.13).
The presence of stress (σ) in the plane of as-grown ZnO thin films was evaluated using estimated value of lattice constant c and its variation is also shown in figure 4.13 as a function of growth pressure. The magnitude of stress present in ZnO thin film was found to decrease from 5.90x10^{10} to 2.91x10^{10} dynes/cm^2 with decrease in sputtering pressure from 40 to 20 mT and thereafter shows an increase (4.64x10^{10} dynes/cm^2) with further decrease in pressure to 10 mT (Fig.4.13). The negative sign of stress obtained for all deposited ZnO thin films is due to large value of lattice constant c as compared to the corresponding value reported for ZnO single crystal and the unit cells are under the state of elongation. It may be recalled that ZnO films deposited at low sputtering pressure (10 mT) had a high level of stress due to extensive bombardment of energetic sputtered particles on the film surface. The increase in stress with increasing sputtering pressure (> 20 mT) may be attributed to the presence of porous and rough microstructure [Menon et. al., 2008]. The processing of ZnO thin film under reactive (mixer of argon and oxygen) atmosphere at low sputtering pressure (10 mT) may induce defects at the interstitial site or grain boundaries, resulting in the elongation of c axis, thus giving higher magnitude of stress.

The average crystallite size of ZnO thin films estimated from the full width at half maximum (FWHM) of (002) XRD peak using the well-known Scherrer’s formula
[Menon et. al., 2008], is presented in figure 4.14 as a function of growth pressure. The estimated value of crystallite size for all prepared ZnO thin films is in the range 9 to 17 nm. Crystallite size is found to be maximum (~ 17 nm) for the thin film deposited at 20 mT and decreases on either increasing (> 20 mT) or decreasing (10 mT) the sputtering pressure (Fig.4.14). Optimum growth condition is essentially required for providing the nucleating centres and subsequent settlement of sputtered species with proper grain growth thereby giving ZnO thin film with maximum crystallite size at 20 mT sputtering pressure. Figure 4.15 shows the AFM images of the surface of ZnO thin films grown at different sputtering pressure (10 to 40 mT) under reactive gas composition of 50% oxygen and 50% argon. The surface morphology of the deposited ZnO thin films were fine having uniformly distributed crystallites except for the film deposited at 30 mT. However, the film deposited at 20 mT is uniform having large grain size and is in agreement with XRD results. The variation of surface roughness of ZnO thin film with sputtering pressure is also shown in figure 4.14. It can be seen from figure 4.14 that ZnO thin films deposited at lower pressure (≤ 20 mT) were smooth having small surface roughness (~ 3 nm), and becomes very rough (> 5 nm) at higher growth pressures (≥ 30 mT). The observation of rough microstructure of ZnO thin film deposited by rf sputtering at higher pressure is in agreement with the reports available in the literature by various workers [Gupta and Mansingh, 1996; Menon et. al., 2008].

![Figure 4.14: Variation of crystallite size and surface roughness of ZnO thin films as a function of sputtering pressures](image)

4-30
Figure 4.15: AFM images of the surface of as-grown ZnO thin films deposited at (a) 10 mT, (b) 20 mT, (c) 30 mT and (d) 40 mT

4.6.2 Optical Studies

The UV-Visible transmission spectra of ZnO thin films of 40 nm thickness deposited at different sputtering pressures (10 to 40 mT) are shown in figure 4.16. All films were highly transparent (Fig.4.16) in the visible region having transmission in the range (75 to 90%). The sharp fundamental absorption edge was observed for all prepared ZnO thin films and was found to shift towards lower wavelength with increase in the sputtering pressure (Fig.4.16). The optical bandgap $E_g$ of the sputtered thin films were estimated from the linear portion of plot between $(\alpha h\nu)^2$ versus $h\nu$, where $\alpha$ is the absorption coefficient, $h$ is the planck's constant and $\nu$ is the photon energy. Variation of the estimated values of bandgap of ZnO thin film is shown in the inset of figure 4.16 as a function of growth pressure. The band gap was found to decrease from 3.65 eV to 3.55 eV with increase in sputtering pressure from 10 to 40 mT (Inset of Fig.4.16). The obtained values of band gap are in well agreement to the corresponding values reported by other workers for ZnO film grown by rf sputtering [Menon et. al., 2008; Gupta and Mansingh, 1996].
Figure 4.16: UV-visible transmission spectra of the as grown ZnO thin films grown at different sputtering pressures (10 to 40 mT). Inset shows the variation of band gap of the ZnO thin films as a function of growth pressure.

Fourier transform infra-red (FTIR) spectra of ZnO thin films deposited at different growth pressures are shown in figure 4.17. A strong absorption band in the region 410 cm$^{-1}$ corresponding to $E_1$(TO) mode, was observed in all FTIR spectra which is in agreement with earlier reports for ZnO films and bulk confirming the formation of Zn–O bond in the present work [Menon et. al., 2011].

Figure 4.17: Fourier Transform Infra Red spectra (FTIR) spectra of ZnO thin films deposited at different sputtering pressure (10 to 40 mT)
No significant shift in the position of $E_1$ (TO) mode was observed for ZnO thin films grown at different sputtering pressure. The frequency of absorption mode of a material depends on the relative masses of constituent atoms, force constants of the bonds, and relative arrangement of the atoms [Menon et. al., 2011]. The estimated value of force constant and bond energy using $E_1$ (TO) absorption mode was estimated to be about 133 N/m and 4.9 KJ/mol respectively ZnO thin film deposited at different sputtering pressure.

### 4.6.3 Sensing Response towards Liquor Ammonia

The sensing response characteristics of SAW sensor having 40 nm thin ZnO sensing layer (deposited under different sputtering pressure) for the headspace vapors of liquor ammonia (25%) is shown in figure 4.18. The exposure time of liquor ammonia with the surface of SAW sensors was fixed at 1.5 minutes. Two cycles have been shown for the ZnO films deposited at different pressures in figure 4.18., indicating good reproducibility of prepared SAW gas sensors.

![Figure 4.18: Sensing response of SAW sensor having chemical interface of ZnO thin films deposited at different pressures (10 to 40 mT) to liquor NH$_3$ vapors. The baseline of the sensor was offset to zero frequency before measurements](image)

The behaviour of sensing response towards liquor ammonia was found to be similar to that observed in figure 4.6 for ZnO/SAW sensors having different thickness of sensing layer. During interaction of target vapors, initially a negative shift in differential frequency ($-S_a$) followed by a much higher positive shift in differential frequency ($+S_a$)
has been observed for all prepared SAW sensors having ZnO sensing layer deposited at different growth pressures (Fig.4.18). Similarly, during removal of target vapors, the positive shift in differential frequency overshoots to the negative side (Fig.4.18) before settling at the base line value \((\Delta f_a = f_0 - f_\text{s} = 0)\). The values of \(-S_a\) and \(+S_a\) (measured from baseline) obtained during the first cycle of vapor interaction with ZnO/SAW sensors are plotted in figure 4.19 with deposition pressure of ZnO sensing layer. The SAW sensor having ZnO thin film grown at 20 mT sputtering pressure (Fig.4.19) was found to exhibit both the maximum value of \(|+S_a|\) and minimum magnitude of \(|-S_a|\). However, SAW sensor with ZnO interface layer grown at 30 mT gives maximum magnitude of \(|-S_a|\) and reasonably higher value of \(|+S_a|\).

![Figure 4.19: Variation of initial negative shift \((-S_a)\) and positive shift \((+S_a)\) in differential frequency towards liquor ammonia for SAW sensor having ZnO chemical interface film deposited under different pressures](image)

The response time and recovery time of the SAW sensors having chemical interface of ZnO thin films deposited at different pressures (10 to 40 mT) with exposure to liquor ammonia is shown in Table 4.3. The SAW sensor with ZnO film deposited at 20 mT shows a fast response time (21 s) and recovery time (180 s). The sensors having ZnO thin films grown at higher pressures (30 mT and 40 mT) are unable to recover fully to the baseline value \((\Delta f_a = 0)\) and show a drift in the baseline after first cycle (Fig.4.18). However, these sensors (ZnO film grown at 30 mT and 40 mT) recover fully the initial
baseline frequency after prolonged time (few hours) by purging in nitrogen. It is important to note that the SAW sensors with ZnO thin films deposited at lower pressure (10 and 20 mT) were able to recover fully the baseline showing reproducible and reliable response (Table 4.3). The observed response behavior may be related to the microstructure of the sensing layer. ZnO thin films grown at higher pressures (30 mT and 40 mT) possess porous and rough microstructure. The ammonia molecules are expected to diffuse deep inside the sensing layer and take a longer time to recover back the initial baseline under continuous flow of N₂ carrier gas. While porosity of the ZnO sensing layer deposited at low pressure (10 and 20 mT), is expected to be just enough to allow the ammonia gas molecules to interact fast with its surface and leave quickly (Table 4.3) after removing the target gas from the system (fast recovery time).

Table 4.3: The response time and recovery time of the SAW sensors having chemical interface of ZnO thin films deposited at different pressures (10 to 40 mT) with exposure to liquor ammonia vapors

<table>
<thead>
<tr>
<th>Sputtering pressure (mT)</th>
<th>Response time (seconds)</th>
<th>Recovery time (seconds)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>30</td>
<td>209</td>
</tr>
<tr>
<td>20</td>
<td>21</td>
<td>180</td>
</tr>
<tr>
<td>30</td>
<td>53</td>
<td>9000</td>
</tr>
<tr>
<td>40</td>
<td>40</td>
<td>1200</td>
</tr>
</tbody>
</table>

4.6.4 Fitting of Mass Loading and Elastic Loading Contributions

As explained earlier, the contribution of acousto-electric interaction to the observed sensing response characteristics is considered to be negligible for ZnO/SAW sensors. The sensing response is expected to be having a combined effect of mass loading and elastic loading. The negative shift in differential frequency (-Sₐ) dominates for initial few seconds followed by a positive shift in the differential frequency (+Sₐ) for longer time in the sensing response towards liquor ammonia. The experimental response data of liquor ammonia obtained for SAW sensors having ZnO sensing layer deposited at different sputtering pressure are fitted independently with equation 4.30 considering a, b, c and d as the fitting parameters. The best fitting of sensing response for ZnO thin films grown at 10, 20, 30 and 40 mT are shown in figure 4.20 (a) to (d) respectively.
\[ S_a = 337.8 \times (1 - \exp(-0.1 \times t)) - 57.96 \times (1 - \exp(-2.48 \times t)) \]

(a)

\[ S_a = 904.1 \times (1 - \exp(-0.155 \times t)) - 394.3 \times (1 - \exp(-0.43 \times t)) \]

(b)
Figure 4.20: Fitting of the sensing response of ZnO/SAW sensors using contributions from both the mass loading and elastic loading for sensing ZnO layer deposited at a) 10 mT b) 20 mT c) 30 mT and d) 40 mT. The individual contribution of mass loading and elastic loading are also shown separately.
The curves showing individual contribution of mass loading and elastic loading towards sensing response are also plotted in figures 4.20 (a) to (d). It may be seen from figure 4.20 (a) to (d) that the mass loading and elastic loading have distinct contributions giving positive shift and negative shift in differential frequency respectively, however, the combined effect of both fits very well to the experimentally obtained sensing response curve of ZnO/SAW sensors towards liquor ammonia. The contributions of both mass loading and elastic loading towards sensing response was found to increase initially with increase in time and thereafter, tends to saturate when liquor ammonia vapors interact with the surface of all prepared SAW sensor structures (Fig.4.20 a to d).

The contributions of both mass loading and elastic loading were found to depend strongly on the processing pressure of sensing layer. The contribution of both the mass loading and elastic loading towards the sensing response of ZnO/SAW sensor for liquor ammonia are plotted in figures 4.21 (a) and (b) respectively as a function of the processing pressure of sensing ZnO thin films. The magnitude of positive shift in differential frequency \(+S_m\) due to mass loading effect alone was found to increase with increase in growth pressure of sensing layer from 10 mT to 20 mT (Fig. 4.21a) and thereafter, shows a continuous decrease with further increase in growth pressure (> 20 mT). Similar effect of elastic loading on the magnitude of negative shift in differential frequency \(-S_e\) with growth pressure was observed (Fig. 4.21b). The ZnO thin film deposited at 20 mT pressure on the surface of SAW resonator shows maximum positive shift as well as negative shift (Fig.4.21a and b). The observed results clearly indicate that the contribution of mass loading and elastic loading towards sensing response depends on the properties of ZnO sensing layer which in turn depends on the growth pressure and the expected correlation between them are discussed in the subsequent sections.
Figure 4.21: Fitted response of ZnO/SAW sensor for ZnO thin films deposited at different sputtering pressures showing contributions of (a) mass loading and (b) elastic loading.
4.6.5 Correlation of Response with Structural Property of ZnO

The interaction of target gas molecules (liquor ammonia) on the surface of ZnO/SAW sensor undergoes various mechanisms which in turn is expected to depend strongly on the microstructural properties of the ZnO thin film. Hence a correlation between the various response parameters such as sensing response ($\pm S_a$) and response/recovery time with the structural properties (grain size, stress, roughness) of the sensing ZnO thin film deposited at different pressures is attempted.

The elastic loading contribution ($-S_e$) towards sensing response was identified to have some correlation with the crystallite size of the sensitive ZnO coating and is shown in figure 4.22a. The magnitude of $-S_e$ was seen to increase slowly with increase in the crystallite size of the ZnO thin film up to 15 nm (Fig.4.22a) and thereafter shows a fast increase with further increase in crystallite size to 17 nm. The presence of bigger size crystallites of the ZnO sensing layer seems to favour the elastic loading contribution ($-S_e$) towards the sensing response of SAW sensors for liquor ammonia. ZnO thin film with bigger size crystallites might be having more void areas at the grain boundaries or surface for the analyte vapor molecules to get trapped. The enhanced interaction of the surface or grain boundaries with large amount of trapped analyte vapors (liquor ammonia) results in the more stiffness of ZnO sensing layer having bigger size crystallites. The stiffening of sensing layer results in increasing the SAW velocity of ZnO/SAW sensor and hence a much higher shift in frequency is observed with the interaction of liquor ammonia due to the contribution of elastic loading (Fig.4.22a). The increase in elasticity of the sensing film due to the trapping of target analyte is in agreement with the results reported by other workers [Hietala et. al., 2001]. ZnO sensing layer deposited at a sputtering pressure of 20 mT possess the maximum size (~17 nm) of crystallites in comparison to that obtained at other pressures and hence show maximum shift in negative differential frequency ($-S_e$) due to elastic loading on interaction with target gas molecules.

The saturated value of positive shift in differential frequency ($+S_m$) due to mass loading contribution was identified to have some correlation with the presence of stress (or lattice expansion) in the ZnO thin film and the observed relation is shown in figure 4.22b.
Figure 4.22: Variation of various sensing parameters of SAW sensor for liquor ammonia as a function of different structural parameters of ZnO thin films: a) $-S_e$ with crystallite size of sensing layer, b) $+S_m$ with stress, and c) Response time and Recovery time with the surface roughness of ZnO film
The value of positive shifts ($+S_m$) were found to decrease linearly from 904 to 338 kHz with increase in the magnitude of stress from $2.9 \times 10^{10}$ to $4.6 \times 10^{10}$ dynes/cm$^2$ in the ZnO thin film and thereafter saturates to a value of about 287 kHz for the sensing layer having large amount of stress ($> 4.6 \times 10^{10}$ dynes/cm$^2$). Hence, mass loading contribution towards the response of ZnO/SAW sensor is more pronounced for the sensing ZnO thin films having minimal stress ($2.9 \times 10^{10}$ dynes/cm$^2$) or maximum lattice relaxation with respect to the corresponding value of bulk ZnO. The ZnO thin film deposited at 20 mT was found to have relaxed unit cell with lattice parameter $c \sim 2.9 \times 10^{10}$ dynes/cm$^2$, and hence exhibits the maximum positive frequency shift ($+S_m$) due to large mass loading contribution (Fig.4.22b). The lattice expansion and the stress in the ZnO thin film is due to the presence of various kinds of defects incorporated while processing of the sensing thin films under extensive bombardment of energetic sputtered species on the substrate surface at lower pressure ($\sim 10$ mT) or due to collision between the various species in the reactive dense plasma at higher pressure ($\geq 30$ mT) [Menon et. al., 2011]. Mass loading is simply the adsorption of target vapor molecules (liquor ammonia) on the surface of sensing ZnO film due to Van der Waals forces and may be influenced by the presence of defects. Therefore, the mass loading contribution towards sensing response is expected to be more for the ZnO/SAW sensors having defect free sensing layer with minimal stress and with more absorption sites for target vapors.

The response time and recovery time of the SAW sensors is expected to influence with the surface roughness of ZnO sensing layer. The variation of response time and recovery time of ZnO/SAW sensor as a function of surface roughness of sensing layer is shown in figure 4.22c. Both response time and recovery time of the SAW sensor was found to increase with increase in surface roughness of the ZnO thin film (Fig.4.22c). The observed results are attributed to the fact that the analyte molecules get trapped and will take more time to adsorb or desorb from the rough surface of the sensing layer. The trapped vapors on the rough surface of ZnO thin film require a large time for desorption and in obtaining the initial base line value (recovery) after removal of target gas. It may be recalled that SAW sensors based on ZnO thin films deposited at higher pressure (30 and 40 mT) recover after a prolonged time due to the formation of a very rough microstructure (Table 4.3).
In summary mass loading contribution towards sensing response of ZnO/SAW sensor increases with increase in the lattice relaxation (minimal stress) whereas the contribution of elastic loading increases with increase in the crystallite size of the sensing ZnO layer. Therefore, the target vapor molecules (liquor ammonia) get trapped initially in the pores or grain boundaries of the sensing ZnO thin film surface, leading to increase in elasticity (stiffness) of the sensing film, thereby giving initially a significant negative shift in differential frequency (Fig.4.6 and 4.18). Subsequently, the vapor molecules get adsorbed on the surface of ZnO thin film, giving the dominant mass loading effects at the later stage with a large positive shift in differential frequency. Similarly during removal of sensing gas (recovery), the vapor molecules adsorbed on ZnO surface get desorbed very quickly but the molecules trapped in the pores or grain boundaries take much more time to get released. Therefore, during recovery of the SAW sensor, differential frequency shift of all the sensors initially overshoots the baseline and shows the negative frequency shifts before reaching the stable base line frequency value (Fig.4.6 and 4.18). The competition between the two contributions (mass loading and elastic loading) causes the observed shifts in differential frequency of SAW sensor as (-Sₐ) and (+Sₐ) at different times of the sensing (response) cycle for liquor ammonia. Elastic loading precedes the mass loading effect, since the target analyte have greater tendency to enter the pores or grain boundaries of the sensing layer rather than adsorption on its surface.

4.7 Effect of Processing Gas Composition

Since reactive gas composition in sputtering chamber is very important to tailor the properties of deposited thin films to a great extent, its effect on the sensing properties of ZnO thin film has been studied. ZnO thin films were deposited simultaneously on the surface of SAW resonator devices and ST-X quartz substrate under varying composition of reactive gas (O₂ and Ar) while keeping the growth pressure (20 mT) and film thickness (40 nm) same. The oxygen percentage in the reactive gas composition was varied from 30% to 100%. The structure and electrical properties of the deposited ZnO thin films and gas sensing response characteristics of ZnO/SAW sensors towards liquor ammonia were obtained and discussed in the subsequent sections.
4.7.1 Structural Property of ZnO Thin Films

XRD pattern of ZnO thin films, deposited under different content of oxygen (30 % to 100 %) in reactive ambient (O₂+Ar) is shown in figure 4.23. The XRD pattern shows reflection corresponding to only (002) plane of wurtzite ZnO structure. It may be seen from the XRD pattern (Fig.4.23) that the position of (002) peak shifts towards the higher angle from 34.09° to 34.32° with increase in the oxygen percentage from 30% to 100% in reactive gas composition.

![XRD pattern of ZnO thin films on ST-X quartz deposited under varying composition of O₂ in reactive gas (O₂ + Ar) mixture](image)

**Figure 4.23**: XRD pattern of ZnO thin films on ST-X quartz deposited under varying composition of O₂ in reactive gas (O₂ + Ar) mixture

The variation of lattice constant (c) and stress in as-deposited ZnO thin film as a function of oxygen percentage in sputtering gas composition is shown in figure 4.24. The lattice constant (5.254 Å) of ZnO thin film grown at lower oxygen content (30%) was much higher in comparison to the corresponding bulk value, indicating that the unit cell is elongated along c-axis and are in tensile stress. The estimated value of lattice constant c was found to decrease continuously from 5.254 Å to 5.225 Å with increase in the oxygen content from 30% to 100% of the gas composition and approaching the bulk values, indicating that the unit cell relaxation occurs with an increase in oxygen content in reactive gas composition (Fig.4.24). The estimated value of stress in the ZnO thin film decreased from 4.2x10¹⁰ to 1.62x10¹⁰ dynes/cm² with increase in oxygen from 30% to 100% in the reactive gas mixture of Ar and O₂ (Fig.4.24). The sign of the stress
for all deposited ZnO film is negative indicating presence of interstitial defects. ZnO thin film grown under oxygen deficient ambient (30% O₂ and 70% Ar) was expected to have large amount of native defects related to Zn interstitials. The presence of Zn interstitials increases the lattice parameter c, of the as-deposited ZnO thin film resulting in elongated unit cell with presence of tensile stress. The growth of sensing layer with increase in oxygen content reduces the Zn interstitial defects, and a defect free ZnO thin film with minimal stress was obtained under 100% oxygen ambient. The value of crystallite size estimated from the (002) XRD peak was found to be almost same (17 nm) for all the ZnO thin films deposited under varying gas composition.

![Figure 4.24](image)

**Figure 4.24:** Variation of lattice constant and magnitude of stress in the ZnO thin films deposited under varying content of oxygen (30% to 100%) in reactive gas composition

Figure 4.25 shows the AFM images of the surface of ZnO thin films grown at different oxygen content reactive gas composition. No significant variation in the crystallite size of the deposited ZnO thin films under varying gas composition is observed and is found to be in accordance with the XRD results. Further no significant variation is observed in the average surface roughness (~ 3.0 nm) of the ZnO thin films deposited with increasing oxygen content in gas composition from 30 to 70% whereas a slight increase in surface roughness (~ 3.2 nm) was observed for ZnO thin film grown under 100% oxygen ambient (Fig.4.25).
4.7.2 Optical Studies

The optical properties of ZnO thin films deposited under varying oxygen content in the reactive gas composition were studied over the wavelength range of 200 to 1100 nm. All deposited ZnO thin films exhibit good optical transmittance (> 80%) in the visible region as shown in figure 4.26. The optical bandgap ($E_g$) of ZnO thin films was evaluated from the Tauc plot as explained earlier and is found to be about 3.21 eV. No significant variation in the value of optical bandgap was obtained for ZnO thin film deposited with varying oxygen content (30% to 100%) in the sputtering gas composition.

FTIR spectra of the ZnO thin films deposited with different content of oxygen in reactive gas composition are shown in figure 4.27. A strong absorption band in the region 410 cm$^{-1}$ corresponding to $E_1$ (TO) mode of ZnO, was observed in the FTIR spectra of all deposited films (Fig.4.27), which is in agreement with earlier reports for ZnO films and bulk confirming the formation of Zn–O bond [Menon et al., 2011].
A shift in the position of $E_1$ (TO) mode towards higher wavenumber was noted from the FTIR spectra of ZnO thin films grown with increase in oxygen percentage from 30% to 100% in reactive gas ambient. The bond energy of Zn-O in the deposited ZnO thin films is evaluated using the FTIR spectra (Fig.4.27), and found to increase from 4.88 to 4.98 kJ/mol with decrease in oxygen content from 100% to 30% in reactive gas composition.
4.7.3 SAW Sensing Response

The sensing response characteristics of SAW sensor having 40 nm thin ZnO film deposited under different oxygen content (30% to 100%) in reactive gas ambient for the headspace vapors of liquor ammonia (25% NH₃) is shown in figure 4.28. Similar to the ZnO/SAW sensors having sensing layer deposited at different pressures or of different thickness (discussed earlier), the sensing layer grown with different reactive gas composition exhibit the distinct sensing response during interaction of target vapors, where an initial negative shift in differential frequency (-Sₐ) followed by a significant positive shift in differential frequency (+Sₐ) shift has been observed (Fig.4.28).

![Figure 4.28](image)

**Figure 4.28**: Sensing response towards liquor ammonia of SAW sensor having chemical interface of ZnO thin films deposited under different oxygen content in reactive gas ambient. The base line frequency of the sensor has been offset to zero frequency

Similarly, during removal of target vapors, +Sₐ overshoots to the negative frequency side before settling at the stable baseline value of frequency (Fig.4.28). It may be noted that baseline frequency \([(Δf)₀ = f₀-f₁]\) of the differential oscillator sensor has been offset to zero frequency before sensing measurements. The sensing response (+Sₐ) of ZnO/SAW sensor with exposure to liquor ammonia vapors (25% NH₃) increases with increase in the oxygen content (30% to 100%) in the reactive gas ambient while processing of sensing ZnO layer (Fig.4.28). ZnO thin film grown in 100% oxygen was
found to exhibit maximum positive shift in differential frequency \( +S_a \approx 991 \text{ kHz} \). No substantial change in the response time (21 s) and recovery time (180 s) of ZnO/SAW sensor for the ZnO thin films deposited in 30%, 50% and 70% oxygen ambient was observed. However a much higher value of the response time (40 s) and recovery time (300 s) was noted for the sensor structure having ZnO sensing layer deposited under 100% \( \text{O}_2 \) gas ambient.

**4.7.4 Mass Loading and Elastic Loading Contributions**

The experimental response data of differential frequency shift \( +S_a \) obtained for SAW sensors having ZnO sensing layer deposited in the different oxygen content in reactive gas composition are fitted to the theory of mass loading and elastic loading contributions using equations 4.27 and 4.28 and taking a, b, c and d as the fitting parameters. The best fitting curves obtained for sensors having ZnO films deposited under varying oxygen content are shown in figure 4.29 (a) to (d). As expected, the contributions of both mass loading and elastic loading towards the shift in differential frequency of SAW sensors have been identified giving positive shift \( +S_m \) and negative frequency shifts \( -S_e \) respectively. The contribution of mass loading and elastic loading towards sensing response has also been plotted separately in figure 4.30 (a) and (b) respectively for all sensing ZnO layer deposited with varying oxygen content (30% to 100%) in reactive atmosphere. It is important to note from figure 4.30a that the contribution of mass loading increases continuously for sensor having ZnO sensing layer grown with increasing content of oxygen (30% to 100%) in reactive sputtered ambient. The saturated value of positive shift in differential frequency \( +S_m \) for ZnO sensing film deposited in 100% \( \text{O}_2 \) was found to be maximum \(-991 \text{ kHz}\) in comparison to that obtained with sensing layer deposited with other gas compositions (Fig.4.29a). The ZnO thin film deposited in oxygen rich environment (100% \( \text{O}_2 \)) is expected to have large amount of oxygen ions on its surface. The presence of oxygen ions provides the large amount of adsorption sites for the target vapors thereby giving maximum mass loading contribution i.e. large positive shift in differential frequency \( +S_m \) for the ZnO/SAW sensors towards liquor ammonia. It is interesting to note from figure 4.30b that the contribution of elastic loading towards the sensing response of SAW sensor remains almost same for all ZnO sensing layers deposited with varying oxygen content (30% to 100%) in reactive sputtered ambient.
\[ S_a = 481.9(1 - \exp(-0.115t)) - 406.6(1 - \exp(-0.18t)) \]

\[ S_a = 904.1(1 - \exp(-0.115t)) - 394.3(1 - \exp(-0.436t)) \]
Figure 4.29: Fitting of the sensing response of ZnO/SAW sensors with mass loading and elastic loading contributions for ZnO thin films deposited at different oxygen content in reactive ambient: a) 30% b) 50% c) 70% and d) 100%. The individual contributions of mass loading and elastic loading towards sensing response are also shown.
The observed behaviour indicates that the trapping of target vapor molecules at grain boundaries or pores of the sensing layer are almost same for all prepared sensors resulting in similar stiffening of sensing layer thus giving saturated value of negative shift ($-S_e$) in differential frequency of about 380 to 400 kHz due to elastic loading (Fig.4.30b).
4.7.5 Correlation of Response with the Properties of ZnO

The magnitude of positive shift in differential frequency (+$S_m$), due to mass loading contribution increases for ZnO films deposited with increase in the content of oxygen in reactive sputtering gas (Fig.4.30a). As explained earlier in section 4.7.4, the contribution of mass loading (+$S_m$) can be correlated with the lattice expansion or stress present in the sensing ZnO layer. The variation of saturated value of (+$S_m$) obtained for ZnO/SAW sensor is shown in figure 4.31a as a function of the stress present in the sensing ZnO layer grown under varying oxygen content in reactive gas ambient. A correlation between the mass loading contribution and stress present in the sensing layer is identified. The contribution of the mass loading towards sensing response of SAW sensor was found to increase with decrease in the magnitude of stress (or relaxation of unit cell) in the sensing layer (Fig.4.31a), and is maximum for the ZnO thin film having minimum amount of stress. However, the increase in adsorption sites for target vapor molecules on the surface of sensing ZnO film grown under 100% O$_2$ may further enhance the contribution of mass loading towards the sensing response. It may be recalled (section 4.7.4) that the elastic loading contribution have some correlation with crystallite size of the sensing ZnO thin film. In the present study no significant change in the crystallite size of ZnO thin films grown under varying oxygen composition in reactive gas ambient was observed, therefore same contribution of elastic loading towards sensing response of all prepared ZnO/SAW sensors was expected (Fig.4.30b). However, a small increase in the magnitude of -$S_e$ for ZnO thin film deposited with decrease in the oxygen partial pressure (Fig.4.30b) was observed and may be related to the change in the bond energy of the Zn-O bond. A variation of the magnitude of -$S_e$ with bond energy is shown in figure 4.31b which shows a linear increase in the magnitude of -$S_e$ with increase in the bond energy. The presence of strong Zn-O bond of sensing layer seems to favour the elastic loading contribution towards the sensing response. No appreciable change in the response time and the recovery time of ZnO/SAW sensors having ZnO film deposited under varying O$_2$ percentage from 30% to 70% in reactive gas composition (30% to 70%) was observed (Fig.4.29) and may be due to insignificant variation in the surface roughness of sensing ZnO thin films, indicating the correlation between the response/recovery time of sensor with surface roughness. The ZnO/SAW sensor having sensing film deposited in 100% oxygen ambient shows increase in the response time (40 s) and the recovery time (300 s), since a slight increase in the surface roughness (3.2 nm) of ZnO sensing layer deposited under 100% O$_2$ gas ambient has been observed.
Figure 4.31: Variation of mass loading and elastic loading contribution towards response of SAW sensor as a function of the structural properties of ZnO thin films deposited at different O₂ percentage in reactive gas composition: a) (+Sₘ) with stress in sensing layer, b) (-Sₑ) with crystallite size of ZnO film

Hence, it may be inferred that the mass loading contribution towards sensing response of a SAW gas sensor is related with the presence of stress in the sensing layer. Sensing layer having minimal stress exhibits a large amount of +Sₘ due to contribution of the
mass loading. Elastic loading contribution is mainly related with the crystallite size of the sensing layer. However, the bond energy of Zn-O bond is also influencing slightly the contribution of elastic loading. Higher the crystallite size and bond energy of Zn-O bond, more will be the elastic loading contribution to the sensing response of SAW sensor. Furthermore, surface roughness of the sensing layer is related to the response and recovery time of the SAW sensor. As the surface roughness of sensing layer increases, target gas molecules will trap deep inside the surface and slow response time and recovery of SAW gas sensor is expected.

4.8 Interaction of Liquor Ammonia: Single Step Process

It may be recalled that ZnO/SAW gas sensor with the interaction of only ammonia vapors in the presence of humidity (or liquor ammonia) gives positive differential frequency shift (+S<sub>a</sub>). All other gases/vapors or their combination with humidity are giving only a negative shift in differential frequency (-S<sub>a</sub>). Since liquor ammonia can be treated as a combination of two molecules, ammonia and water, the observed peculiar sensing response (positive frequency shift) can be due to one of the two possibilities mentioned below:

1. ZnO is highly hygroscopic and therefore water molecules are adsorbed initially on the surface of sensing ZnO film. Subsequently water molecules adsorb ammonia on the surface of ZnO/SAW sensor i.e. interaction of target vapors with SAW sensors is a two step process.
2. Ammonia and water molecules get adsorbed simultaneously on the surface of ZnO/SAW sensor forming ammonium hydroxide i.e. adsorption of target vapors is a single step process.

In order to confirm whether ammonia and water molecules interact with the surface of ZnO coated SAW sensor simultaneously or individually, both are passed sequentially one after the other over the surface of ZnO/SAW sensors. The schematic diagram of set up used for this experiment is shown in figure 4.32, which is an extension of the delivery system shown in figure 3.14 (Chapter 3). The extended system (Fig.4.32) has the capability of passing the target vapors and water vapors sequentially on the surface of SAW gas sensors.
Initially base line of SAW sensors operating in differential oscillator configuration is stabilized under continuous flow of N₂ carrier gas, and offset to zero frequency for sensing measurements. The water vapors are passed over the sensor surface for different periods of time and then dry ammonia in different concentrations is allowed to interact. The sensing response of the SAW sensor was recorded having ZnO sensing layer of different thickness (20, 40 and 80 nm) in differential oscillator mode. The original baseline of the SAW sensor is achieved during recovery cycle by passing N₂ gas. The obtained responses for two concentrations of ammonia 400 ppm and 2400 ppm are shown in figures 4.33 and 4.34 respectively. A negative shift in differential frequency (–Sₐ) of SAW sensor was observed when water vapors interact with its surface (Fig.4.33). The magnitude of –Sₐ was found to increase slightly with the passage of dry ammonia (400 ppm). However, no positive shift in differential frequency (+Sₐ) of ZnO/SAW sensor was found with respect to the baseline for both water vapors and dry ammonia (Fig.4.33). Water vapors were passed on the surface of ZnO/SAW sensors even for different duration (from 0.5 to 50 s) followed by dry ammonia, but still no positive shift in differential frequency (+Sₐ) was obtained in any case. Further the concentration of dry ammonia was also increased to higher concentration 2400 ppm and the duration of passage of water vapors on the surface of all prepared ZnO/SAW sensors were varied up to 60 s and obtained responses are shown in figure 4.34.
Figure 4.33: Response of ZnO/SAW sensors having different thickness (20, 40 and 80 nm) of sensing layer towards sequential interaction of water vapors (different duration) and ammonia (400 ppm)

Figure 4.34: Response of ZnO/SAW sensors having different thickness (20, 40 and 80 nm) of sensing layer towards sequential interaction of water vapors (different duration) and ammonia (2400 ppm)
However, only negative shift in differential frequency ($-S_a$) were observed for ZnO/SAW sensors in all the sequential combinations of water vapors and dry ammonia (Fig.4.34), and no indication of any positive shift ($+S_a$) is observed. Therefore the observed peculiar sensing response ($+S_a$) for liquor ammonia is not associated with the two step process of the sequential interaction of water vapors and dry ammonia with ZnO/SAW sensor surface. It may be inferred that the absorption of liquor ammonia is a single step process of simultaneous interaction of water vapor and dry ammonia with sensing ZnO layer thereby forming ammonium hydroxide. The simultaneous absorption of both ammonia and water molecules on the surface of ZnO thin film coated SAW sensors give positive differential frequency shifts ($+S_a$).

**4.9 Sensing Mechanism Model for ZnO/SAW Sensor**

It may be recalled that ZnO/SAW sensor exhibits a ($-S_a$) for both dry ammonia gas and water vapors individually, whereas the combination of both vapors gives a significant value of ($+S_a$) after getting a small ($-S_a$). The positive shift in difference frequency (response) of ZnO/SAW sensor is mainly due to interaction of liquor ammonia vapors (ammonium hydroxide) rather than the interaction of individual molecules of dry ammonia and water. The phenomenon happening on the surface of sensing ZnO thin film during the interaction of liquor ammonia vapors can be visualized with a simple model as shown in figure 4.35. It may be noted that ZnO is hygroscopic having high affinity towards water vapors and water vapors has good affinity towards ammonia. Consider that the liquor ammonia (AB) vapors consist of two individual molecules, ammonia (A) and water (B) having good affinity towards each other. The effective surface of the sensing thin film (ZnO) before exposure to target vapors is shown schematically in figure 35a. The presence of grain boundary and voids between the crystallite along with rough surface could be clearly seen in the sensing layer (Fig.4.35a), which act as trapping centres for the target vapors. When liquor ammonia vapors are delivered to the surface of ZnO/SAW sensor, the molecules A and B remain separated initially (before interaction) due to difference in their volatility.

During interaction of target vapors with ZnO/SAW sensor, the molecules A or B get trapped at the pores or grain boundaries available near the surface of sensing ZnO thin
film as shown in figure 4.35b. The concentration of unfilled pores gets reduced significantly with increase in interaction time of target vapors (Fig.4.35c). As a consequence, the contribution of elastic loading (-$S_e$) towards the sensing response of ZnO/SAW sensors increases with little contribution from mass loading (+$S_m$<<-$S_e$). Subsequently, the target vapor molecules (A and B) gets adsorbed on the surface of sensing (ZnO) layer freely leading to increase in the contribution of mass loading (+$S_m$>>-$S_e$) towards sensing response at a later time as shown in figure 4.35d. Because of the high affinity, molecules A and B start accumulating and even may form multilayers on the surface of ZnO thin film (Fig.4.35d). Ammonia molecules attract water vapors readily through hydrogen bond forming ammonium hydroxide on the surface of ZnO sensing layer [Shingaya et. al., 1999]. The formation (or reformation in case of liquor ammonia) of ammonium hydroxide on the surface of sensing ZnO thin film, causes a large positive shift in the differential frequency (+$S_a$) of ZnO/SAW sensor.

Figure 4.35: Schematic of the interaction of liquor ammonia molecules with the surface of sensing ZnO thin film a) bare ZnO thin film, b) trapping of molecules A and B at pores, c) reduction in concentration of unfilled pores, and d) adsorption of molecules on ZnO surface
4.10 Conclusions

The sensing mechanism for the distinct response of fabricated SAW sensor having ZnO sensing layer towards liquor ammonia is investigated. Acousto-electric interaction, mass loading and change in elasticity of the sensing film are known to be the major contributions towards the sensing response of SAW sensor. Independent measurements of resistance and capacitance of sensing layer confirm that acousto-electric interaction is not giving significant contribution to the sensing response of ZnO/SAW sensor towards liquor ammonia. Instead contributions of mass loading and elastic loading are dominating the sensing response of ZnO/SAW sensors having ZnO sensing layer deposited under varying conditions (sputtering pressure and gas composition) of different thicknesses. The contribution of mass loading and elastic loading towards sensing response of liquor ammonia has been identified using theoretical fitting of obtained response data. The contribution of mass loading is dominant for the sensing layer having minimal stress, whereas the sensing layer with large crystallite size and strong Zn-O bond favours the elastic loading contribution. The surface roughness of sensing layer is identified to be crucial for the response time and recovery time of the ZnO/SAW gas sensor. A model is proposed to explain the distinct sensing behaviour of liquor ammonia using ZnO thin film based SAW sensor, where adsorption of ammonia and water molecules is considered as a single step process.