5.0 Introduction:

To validate the developed processes and in turn achieve the desired objectives of the research work, a mask for SAW device was fabricated using developed process as explained in previous Chapters and then used the same photomask for fabrication of a SAW sensor. The device targeted to be fabricated was a 500 MHz SAW Resonator.

5.1 SAW resonator design and layout:

The resonator as explained in previous chapters, is based on standing surface waves. These can be configured to act as narrow band resonant circuits by arranging for incident and reflected travelling wave components to interfere with each other in a coherent manner. Fig. 5.1 shows a schematic layout of a two port SAW resonator. In operation, surface waves emitted from both sides of excited IDT are constructively reflected at center frequency by two SAW reflecting gratings, to form standing waves. These are characterized in terms of amplitude or of piezoelectric surface potential.

The elements of SAW reflection gratings comprise of periodic discontinuities. These consist of open thin metal strips. The number of strips required for near total reflectivity depends on reflection mechanism. In case of materials with high coupling co-efficient e.g. Lithium Niobate substrate, total reflection is achieved by few metal strips. In case of low coupling co-efficient materials e.g. ST-quartz substrate, a few thousand grating elements are required to achieve a reflection coefficient close to unity. To keep device size realistic, SAW resonator designs on quartz substrates are normally used for frequencies above 100 MHz.
Reflection of SAW waves from a reflection grating is maximum at center frequency, for which all of individual reflections are additive, there is a narrow frequency range over which the grating reflects SAW waves with reduced efficiency. The width of this grating stop band can be specified as the frequency range over which the grating reflection coefficient exceeds some minimum value. This specification depends on design parameters including type of substrate, type of reflection grating, no. of reflector elements and other losses in grating structure [2].

Design layout of the photomask fabricated for validation of the developed processes is shown in Fig. 5.2. Each tile of this photomask comprises of a SAW resonator structure to be fabricated for chemical/gas sensing applications.

The resonator structure (Fig. 5.3) was designed for Centre frequency 500 MHz and fabricated on ST-quartz. Each reflecting grating of the resonator structure has 200 elements, width of individual grating element being 1.69 micron. The design layout of this resonator was made in AutoCAD and gdsII formats.

Fig. 5.4 shows the expanded view of the structure of a single resonator. The patterns visible in the structure are basically connecting pads. The IDT structure as it constitutes of fine geometries is not visible as the pad geometry is around 500 µm. The incline shown in pad is to avoid electromagnetic feed through. The data generation and verification has to take into account the critical feature size and the different shapes of the pads.

### 5.1.1 Design criticality for SAW resonator mask

As per Campbell [2], “The design of an efficient SAW reflection grating is a necessary but not sufficient criterion for ensuring that the two-port resonator will operate properly. A second criterion of paramount importance relates to placement of
each reflection grating, with respect to its adjacent IDT. Incorrect positioning of either
IDT or grating can degrade the electromechanical transduction between input and/or
output voltages and acoustic resonance to the point where SAW resonance action
can be lost altogether”. It is, therefore, very important that the mask fabricated should
have exact dimensions, so that the resonator fabricated using it works properly.

5.2 SAW resonator photomask fabrication:

The BF mask (Fig. 5.5) was fabricated using the data prepared in dxf (AutoCAD) and
gdsii. This data was verified using Convert
software, converted and transferred to
controller of LASER Pattern Generator
(Heidelberg: DWL 200) for writing it on the
chrome blank. The converted Resonator data
is shown in Fig. 5.6. The mask exposure was
done with 2 mm Write Head using the
optimized writing process given in chapter 2.

The Resist (AZ1518) coated pre baked master grade
chrome blank of size 4"X4" was
used for writing the resonator
pattern. After exposure, the mask
plate was developed for 60 s using
PPD-455 developer. The
developed images are presented
in Fig. 5.7. The pattern was
inspected and subsequently,
residual photoresist descumming,
chromium/chromium oxide etching,
photoresist stripping and cleaning of
the photomask was done using the
optimized processes described in
chapter 4. The fabricated resonator
photomask was (Fig. 5.5 finally inspected for quality and checked for compliance to the design specifications. The developed and etched images of the resonator structures are presented in Figs. 5.7 and 5.8.

The SEM analysis for measurement of CD of fabricated SAW resonator mask (etched) was carried out using Zeiss SUPRA 55 SEM. The SEM images of both developed and etched structures of fabricated photomasks are presented in Fig. 5.9 and Fig. 5.10.

The line widths of the fabricated structures as obtained from SEM measurements, were found to vary from 1.720 µm and 1.682 µm; a deviation of only 8nm to 30nm from the design value of 1.69 µm. Since, this deviation was well within the acceptable design tolerance of 5% or 0.1 µm, the process developed for the fabrication was established as a perfect process for fabrication of photomask for SAW device application.

The developed process of photomask fabrication was further validated by fabricating SAW resonator for use as gas sensor using the fabricated resonator photomask.

5.3 Process validation by fabricating SAW Resonator:

Standard photolithography (PLG) technique shown in Fig. 5.11, was used for fabrication of a SAW resonator, wherein the resonator structures were transferred from photomask to substrate.
High purity aluminum (99.999 %) was deposited on bare 3" diameter quartz substrate using thermal evaporation system (Hind Hivac). The coated thickness was controlled to 2000 Å by using a thickness monitor. Next, substrate was coated with AZ 1505 positive photo-resist using spin coater to a thickness of 1 µm. Post photoresist coating, substrate was pre-baked at 90°C for 30 min to dry solvents and enhance adhesion in an Oven.

The substrate was exposed using i-line (365 nm) mask aligner (MJB3, Karl Suss) through photo-mask for transferring the resonator structures to the photoresist on the substrate. The exposed photo-resist was developed and examined under microscope. Post baking of the developed substrate was carried out at 90°C to dry the developer for about 30 min prior to examination. The exposed aluminum in between the photo-resist was then etched by an electrochemical etching process. Finally the photo-resist was cleaned by Acetone. The pictures of the fabricated devices are shown in Fig. 5.12. The devices were then diced out of the wafer in set of two (for dual device configuration) using dicing machine and the diced chips were packaged. The device pads were bonded to the package pins using 1 mil aluminum wire.

5.3.1 Performance of SAW resonator:

The individual fabricated resonator device were tested for their performance. Each fabricated SAW resonator was subjected to measurement of gain and phase in Vector Network Analyser (ZVR-Rohde and Schwarz). The resonance pattern is
The acoustic resonance in SAW resonator occurs when the total phase shift of the surface wave is $\phi=2\pi n$ within the cavity bounded by two reflection gratings. The resonance was observed at 505.7 MHz, although the device was designed to operate at 500 MHz. This is because design and fabrication of a SAW device is very complex and many factors need to be modelled/optimized. However, the resonance was observed in fabricated device, it means that the position of all elements in reflector gratings was perfect on mask (and on device). This is very important aspect of resonators, if positions of grating elements are not proper, the standing waves do not form on the surface. Thus validates the process of mask fabrication.

5.4 SAW based gas sensors:

SAW devices can be used to monitor/sense gases and organic solvents, if these are coated with a material which selectively adsorbs molecules from air [3-6]. In a SAW based chemical sensor, either a delay line or a resonator is inserted into feedback loop of a two port oscillator, whose frequency then depends on the number of molecules adsorbed. A delayline is the simplest structure made of two inter-digital transducers (IDT). For IDT, located sufficiently far apart, the free substrate surface between them offers uniform adhesion conditions for the chemically sensitive coating. A delayline needs automatic gain control and matching to demonstrate tolerable insertion attenuation.

The resonators in contrast have small attenuation than most delay lines and do not need any matching. The oscillator design is simple as compared with delay line in terms of phase change.

The elements of SAW reflection gratings comprise of periodic discontinuities. These consist of open thin metal strips. The no. of strips required for near total reflectivity depends on reflection mechanism. In case of dominant piezoelectric shortening e.g. Lithium Niobate substrate, total reflection is achieved by few metal
strips. In case of dominant mass loading e.g. ST-quartz substrate of, a few thousand grating elements are required to achieve a reflection coefficient close to unity.

Reflection of SAW waves from a reflection grating is maximum at center frequency, for which all of individual reflections are additive, there is a narrow frequency range over which the grating reflects SAW waves with reduced efficiency. The width of this grating stop band can be specified as the frequency range over which the grating reflection coefficient exceeds some minimum value. This specification depends on design parameters including type of substrate, type of reflection grating, no. of reflector elements and other losses in grating structure [2]. As per Campbell [2], “The design of an efficient SAW reflection grating is a necessary but not sufficient criterion for ensuring that the two-port resonator will operate properly. A second criterion of paramount importance relates to placement of each reflection grating, with respect to its adjacent IDT. Incorrect positioning of either IDT or grating can degrade the electromechanical transduction between input and/or output voltages and acoustic resonance to the point where SAW resonance action can be lost altogether”.

SAW sensors operate at frequencies of MHz to low GHz range to measure physical, chemical or biological quantities. Their high sensitivity makes them attractive for chemical vapour detection and gas sensing. In many cases, the output of these sensors is a frequency, which can be measured simply with an electronic counter. With proper design, these sensors can be quite stable permitting a large dynamic range to be realized.

5.5 Measurement methods:

For a passive delay line, the phase shift between input and output transducers, separated by a known distance, gives the velocity. For resonator or delay line oscillators, the oscillator frequency is usually desired, which can be measured easily and precisely with a digital counter.

5.6 Chemical warfare agents:

The threat of terrorist activity has risen significantly all over the world, after the massive terrorist attack against USA on September 11, 2001. One of main concerns is the potential use of weapons of mass destruction, such as chemical weapons against civilians. Utilizing sensor technology, the protection of society can be
significantly enhanced as the technology facilitates continuous monitoring, surveillance and warning systems.

Exposure to chemical agents acts via the skin (liquid and high vapour concentrations), eyes (liquid or vapour) and respiratory tract (vapour inhalation). At ambient temperature and pressure most chemical agents are in the liquid form. After the detonation or with the increased temperature most agents are dispersed as suspensions of fine liquid droplets. The most volatile agents are cyanides and phosgene and the least volatile are sulphur mustard and VX (O-ethyl-S-[2-isopropylaminoethyl methyl phosphothiolate). Kikilo et al [14] have given a detailed account of chemistry of chemical warfare agents. Practically, the vapour of all chemical agents, with the exception of hydrogen cyanide is heavier than air. Therefore they tend to remain in the lowest point of the affected area.

If the chemical warfare agents are able to evaporate within 24 hours, they are classified as non-persistent and if they tend to remain in the environment for more than 24 hours, they are called persistent. Volatile agents pose the dual risk of dermal and inhalation exposure, while persistent liquids are more likely to be absorbed across the skin.

Chemical warfare agents can also be divided into lethal and incapacitating agents. A substance is considered to be incapacitating if less than 0.01 of the lethal dose causes incapacitation, such as nausea or visual problems. The injury caused by the chemical agent is measured as the concentration-time product (Ct). Ct is the concentration of the chemical agent detected in the air multiplied by the time than an individual is exposed to that concentration. Additionally, LCt50, is the Ct of an aerosol or vapour that will result in clinical effects in 50% of the exposed population [15].

5.7 Classification and toxicological properties:

Vesicating and blistering agents:

Vesicants cause extensive irreversible damage to tissues within minutes of exposure. Vesicants are also known as blister agents. The most clinical effects of vesicants are swelling and blisters on the skin, irritation, conjunctivitis, corneal capacity and other major damage to the eyes as well as respiratory damage. Sulphur mustard (Cl(CH₂)₂S(CH₂)Cl) is such a vesicant agent.
Chocking agents or pulmonary intoxicants:

Inhalation is the route for the pulmonary intoxicants. The latent period of phosgene and chlorine may last from minutes to several hours depending on the concentration as well as the duration of exposure and the physical activity of the exposed person. Phosgene (COCl₂) (CG) is a chocking agent.

Nerve agents:

There are two categories of nerve agents: G agents and VX agents. G stands for German- such as Tabun (GA), Sarin(GB), Soman (GD), Cyclosarin (GF). G agents are vapours at ambient temperatures and VX agents are liquids. Nerve agents are organo-phosphates and act at cholinergic synapses. They affect central nervous system. They are easily absorbed through the skin, eyes and lungs. Tabun, Sarin and Soman and VX are dangerous nerve agents.

5.8 Surface Acoustic Wave sensor:

Surface Acoustic Wave (SAW) sensor is based on the adsorbed mass while the adsorption mechanism is the physical interaction between the sensor surface and an analytic. This physical basis attracts for the detection of high molecular mass species, such as persistent CWAs. Bulk and surface acoustic wave resonators have also been used extensively in the design of multifunctional physical and chemical sensors, including microbalances, viscosity sensors, humidity sensors, immune detectors, gas sensors and magnetic and electric field sensors [16].

The surface acoustic wave (SAW) sensor is the most popular for selective sensing of chemical warfare agents [17-22]. It was first mentioned in 1979 by Wohltjen and Dessy [11]. It is based on the GC piezoelectric response demonstrated by King in 1964 [8] and is used for detection of variety of organic gases [23-24]. The basic principle of a SAW gas sensor is that it relies on propagating or standing acoustic wave, i.e., a surface acoustic wave is electrically excited in a piezoelectric plate substrate by use of the metallic inter-digital transducer (IDT) and is detected by another IDT located at the other end of the material. The SAW sensor device is then used as at frequency-selective Component in an oscillator circuit. This enables recording of the sensor response with an outstanding accuracy [25-27].
Sensing is a reversible adsorption of chemical vapor by a specific organic or inorganic material coating, which is sensitive and selective to target gases. Chemical interaction of the acoustic wave with the surrounding environment at the sensor surface causes changes in velocity and amplitude of the wave. Adsorption of gaseous analyte into the sensitive layer causes an increase of the coatings mass and consequent decrease in the acoustic wave’s velocity. Consequently, frequency of the oscillator decreases.

5.8.1 Advantages:

The main advantage of SAW sensors is their small size and apparently low power consumption due to low operating temperature. Additionally, they offer inherent high sensitivity, resolution and stability. Advantages also include a wide measurement range of the chemical components, relatively low cost and availability of integrated electronic circuitries. Additionally, SAW sensors show an excellent linearity of the calibration curve for each analyte and high flexibility towards the analytes of choice due to the use of "semi-selective" polymer coatings [28]. They are able to detect analytes at ambient temperatures and are suitable for measurements in inert atmosphere as well as ambient conditions even when the humidity is high. SAW sensors are reported to be highly selective, which is achieved with an array of different coatings on individual sensors [12].

5.9 SAW Sensor for Sarin (DMMP) sensing fabricated under current study:

Use of SAW devices for detection/sensing of Chemicals/ explosives/chemical warfare agents (Sarin through DMMP) has been an active area of study [29-37]. A SAW resonator based Sarin (DMMP) sensor was fabricated using the fabricated resonator devices.

5.9.1 Fabrication of SAW resonator sensor:

The resonator device was cleaned using Oxygen plasma in a Plasma Asher. SAW device was then coated with Bisphenol polymer by drop dry method using methanol as a solvent in a clean room environment at room temperature. The amount of material loaded was about 50 ng on the SAW path between the IDTs. The device was then baked at 100°C for 5 hours in nitrogen flow to evaporate remaining solvent. The device along with the package was then fitted to a sensor cell for flowing vapours in and out as described by Nimal et al. [38]. The devices were placed in the
feedback loop of two stage amplifier in order to be realized as sensor oscillators. The outputs of the two oscillators, the reference and the sensor were mixed using a double balanced IC mixer and filtered by a passive low pass filter. The output was in kHz frequency which was amplified and passed to digital section for frequency measurement [38]. The vapor generator system for sensor characterization [39] was used. Nitrogen was used as carrier gas and the vapor was generated by flowing nitrogen through a flask placed with a permeation vial containing DMMP (Di-Methyl Methyl Phosphonate, a simulant of Chemical Warfare Agent Sarin. The sensor was exposed alternately to carrier gas and a mixture of carrier gas and DMMP vapors.

5.9.2 Performance of SAW resonator sensor for Sarin (DMMP):

The performance of fabricated devices as chemical (Sarin-DMMP) sensor was studied. The SAW device gas sensor was characterized using Vector Network Analyser (ZVR-Rohde and Schwarz). Fig. 5.14 shows typical sensing curve of the prepared SAW sensor with exposure to 3 ppm DMMP vapor. A frequency shift of 700 Hz was obtained, indicating sensitivity of 233 Hz/ppm.

Fischerauer et al [40] have studied the performance of a chemical sensor (SAW resonator) operating at 434 MHz. Dickert et al [40] in their study of a SAW resonator sensor for Toluene (433 MHz and 1 GHz) have inferred that limits of detection can be lowered by increasing the oscillation frequency of device. However, higher frequencies need thinner polymer coatings for detection. Their sensor response was 61 kHz/1000 ppm (61 Hz/ppm). Our sensor has demonstrated a frequency shift of 700 Hz for 3 ppm (about 233 Hz/ppm). Liu et al [33] have described a SAW resonator sensor for 500 MHz on ST-quartz for detection of formaldehyde. Chen et al [41] have studied a two-port SAW resonator device on ST-quartz substrates at 200 MHz for detection of mustard gas and
reported sensitivity of 106 Hz/ppm. Li et al [42] have theoretically analyzed two port resonator based SAW sensor and have concluded that it is necessary to properly choose the width, the thickness and material parameters of the sensitive film in addition to the optimization of device structure, in order to improve detective sensitivity and to reduce the insertion loss.

5.10 Conclusion:

A photomask was fabricated for SAW resonator. The designed CD size was 1.69 micron. The fabricated CD was measured as 1.6 – 1.7 in microscope. The same CD was measured between 1.720 and 1.682 mm in SEM (difference from CD: 8 to 30 nm - within tolerance limit of 5% or 0.1µm), thus validating the process for mask fabrication.

A SAW resonator device designed for operation at 500 MHz was fabricated using the mask and studied for use as chemical (Sarin-DMMP) sensor. The frequency response of the fabricated SAW resonator device showed excellent match (insertion loss within 6 dB) as required for SAW resonator. The resonance was observed at 505.7 MHz. A DMMP sensor (for Sarin) was fabricated from SAW resonator device. Sensing curve of the prepared SAW sensor with exposure to 3 ppm DMMP vapors demonstrated a frequency shift of 700Hz. Bisphenol polymer coated SAW sensors can be used for sensing DMMP vapors, with proper integrated electronics. This validates the process for mask fabrication.
5.11 References:


