SUMMARY, CONCLUSIONS AND SCOPE FOR FUTURE WORK

The main objective of the present work was to study the effect of DC reactive magnetron sputtering on the deposition of compound film like zirconium nitride (ZrN). This has been systematically studied starting from performance evaluation of the magnetron cathode, plasma analysis of the glow discharge to determine plasma parameter, study on the reactive magnetron sputtering process and thus to prepare good zirconium nitride films. Its characterization such as electrical, optical and structural properties of the as-deposited and annealed films was studied. As an application, zirconium nitride films have been used in metal-semiconductor (M-S) structure as electrode and as a top-level electrode in metal-oxide-semiconductor (MOS) and metal-insulator-metal (MIM) structures.

A DC reactive magnetron assembly, which could accommodate a 100 mm diameter cathode, was used in the present investigation. The reactive magnetron sputter deposition has been characterized by studying the glow discharge characteristics of the zirconium cathode first only in argon and then later in both argon and nitrogen environment. The glow discharge characteristics show three different regions of cathode potential regime for different discharge currents and nitrogen partial pressures. The variation of cathode potential has been explained on the basis of negative ion formation and cathode poisoning effects.

Zirconium nitride films were prepared by DC reactive magnetron sputtering from a pure Zirconium (99.9%) disk of 100 mm diameter target onto cleaned glass and p-type silicon substrate (100 orientation and $\rho = 10 \Omega \text{cm}$). The pumping system was capable of providing an ultimate vacuum of $2 \times 10^{-5}$ mbar. Nitrogen (99.99%) and Argon (99.99%) was used as reactive and sputtering gasses, respectively. Nitrogen partial pressures were varied from $4 \times 10^{-5}$ mbar to $10 \times 10^{-5}$ mbar and the effect on the structural, electrical and optical properties of the films was systematically studied.

XRD results showed that the films were deposited at room temperature that were crystalline in nature with (111) and (121) orientation for nitrogen partial pressure beyond $6 \times 10^{-5}$ mbar. Electrical resistivity of the ZrN films varied from $1.72 \times 10^{-3} \Omega \text{cm}$ to $48.28 \times 10^{-3} \Omega \text{cm}$ with increase in nitrogen partial pressure from 6-
In order to obtain good metallic ZrN films with less resistivity, we fixed nitrogen partial pressure for our further study at 6×10⁻⁵ mbar. Films deposited at room temperature at nitrogen partial pressure of 6×10⁻⁵ mbar were crystalline in nature with cubic (111) orientation. The refractive index and extinction coefficient were found to be 1.95 and 0.43, respectively.

ZrN films (1800 Å thickness) were deposited on p-type silicon substrate at room temperature, and the films were uniform, adhesive and void free. In order to study the annealing effects of ZrN films, films deposited at room temperature were subjected to post annealing in a muffle furnace at 350 °C and 550 °C for 1 hour in air. Annealed ZrN/Si films showed polycrystalline nature with cubic (111) and hexagonal (201) phases corresponding to ZrN. It also showed peaks corresponding to those of ZrO₂ and Zr. Intensity of peaks corresponding to (111) and (201) increased with increase in annealing temperature. The grain size for the films annealed at 350 °C was 7.2 nm and it increased to 11.1 nm in case of films annealed at 550 °C. Electrical resistivity was found to increase to 6.21×10⁻³ Ωcm for annealed films. The variation in refractive index and extinction co-efficient was found to be in the range of 1.95-1.80 and 0.43-0.15 for annealed films at 350 nm, respectively.

Scanning electron microscope (SEM) and energy dispersive analysis of x-rays (EDX) was employed to analyse the surface morphology of the films. SEM results showed alloy penetration pits through diffusion process. Metallization was completely destroyed by reactions induced by thermally activated process with the substrate or layers on the top. As annealing temperature increased, silicon from substrate diffused into ZrN through grain-boundary paths to satisfy solubility. Concomitantly, ZrN can also diffuse into the substrate. Thus, as the pit size varied, Si-to-ZrN area contact increased, allowing pits with different sizes to form. Extent of penetration was greater at higher temperature, thus leading to higher diffusion rates and solubility. EDX data taken at the substrate has confirmed SEM analysis.

Two different ZrN/Si structures have been fabricated by depositing ZrN layer on p-type silicon substrate at two different conditions at room temperature, namely Sample-1 and Sample-2.
Sample-1 ZrN/Si Schottky structure was fabricated at an ultimate base pressure of $3.1 \times 10^{-5}$ mbar with a current of 200 mA. Distance between target and substrate was 90 mm with a dark blue colour of ZrN. Rectifying behavior was observed from I-V characteristics with a knee voltage of 0.7 volts and reverse saturation current of 0.2 µA. Barrier height was found to be 0.81 eV with a depletion capacitance in 43-59 pF range.

Sample-2 ZrN/Si Schottky structure was fabricated at an ultimate base pressure of $2.5 \times 10^{-5}$ mbar with a current of 270 mA. The distance between the target and substrate was kept at 110 mm, where ZrN film colour was golden yellow. I-V characteristics showed that the rectifying behavior was with a knee voltage of 0.55 volts and reverse saturation current of 0.1 µA. Barrier height was found to be 0.83 eV. Depletion capacitance was obtained in 1-2.6 nF range.

Further, we have fabricated and characterized ZrN metal-semiconductor contact on n-type germanium and p-type gallium nitride using I-V and C-V techniques at room temperature. ZrN/Ge structure exhibited Schottky nature. However, ZrN/GaN showed linear I-V characteristics with high resistance. For ZrN/Ge Schottky structure, barrier height was found to be 0.61 eV with reverse saturation current of 0.3 mA. Depletion capacitance is found to be in the range of 7-17 pF for ZrN/Ge Schottky structure. Linear ohmic behaviors of ZrN/GaN with high resistance may be due to a thin oxide layer or oxy-nitride layer between metal and semiconductor, thin enough to allow only a small current to flow. Presence of such a layer shall modify the I-V characteristics of the diode. This oxy-nitride layer would be incorporated on to gallium nitride substrate from external environment or when sputtering chamber is exposed to the atmosphere for few minutes before loading the substrate for sputtering.

In order to investigate the surface morphological changes i.e. pits/voids formation of ZrN/Ge and ZrN/GaN, scanning electron microscopy was employed. SEM results indicated that there was no voids/pits formation for the ZrN/Ge structures at room temperature. However, ZrN/GaN structure showed voids/penetration pits
formation at room temperature only whereas voids/penetration pits formation was observed in the ZrN/Si structures when annealed at 350°C and 550°C.

Later, our work proceeded towards fabrication and characterization of ZrN/TiO\textsubscript{2}/p-Si metal-oxide-semiconductor structure. TiO\textsubscript{2} was deposited from pure Titanium (99.9%) disk, under optimized oxygen partial pressure. The electrical characteristics of MOS capacitor have been investigated by current-voltage, capacitance-voltage and capacitance-frequency measurements which were carried out at 100 kHz at room temperature. Flat band capacitances, flat band voltage, leakage current, dielectric breakdown, oxide charge and type of conduction were measured.

C-V curve clearly indicated three distinct regions of a MOS structure i.e., accumulation, depletion and inversion mode with a maximum capacitance of 3pF and minimum capacitance of 2.2pF. The calculated flat band capacitance was found to be 2.86pF, which correspond to flat band voltage of –1.7V. Fixed oxide charged density and interface state density was calculated and was found to be 1.63×10\textsuperscript{10} cm\textsuperscript{-2} and 6.3×10\textsuperscript{11} cm\textsuperscript{-2} eV\textsuperscript{-1}. Total oxide charge was found to be 2.6×10\textsuperscript{-9} C/cm\textsuperscript{3}.

I-V characteristics revealed that the leakage current density was of 0.5 mA/cm\textsuperscript{2} in accumulation mode and 2 mA/cm\textsuperscript{2} in inversion mode at a field of 0.12 MV/cm, respectively. Dielectric breakdown of ZrN/TiO\textsubscript{2}/p-Si structure was found to be 0.12 MV/cm in accumulation mode. DC conduction mechanism revealed that the dominant conduction mechanism prevailing in high field region was identified as space-charge-limited-conduction. Capacitance-frequency characteristic indicated a decrease in capacitance as frequency increased.

To compare ZrN electrode MOS structure with standard metallized MOS capacitor, Al/TiO\textsubscript{2}/p-Si MOS structure was fabricated and characterized. The maximum capacitance of 321pF was observed in accumulation mode whereas minimum capacitance of 147pF was observed in inversion mode. Flat band capacitance was found to be 274.5 pF, which corresponds to flat band voltage of –0.2V. Fixed charge density of 2.04×10\textsuperscript{11} cm\textsuperscript{-2} and interface state density of 7.93×10\textsuperscript{12} cm\textsuperscript{-2} eV\textsuperscript{-1} was determined from C-V curve. I-V characteristics revealed a leakage current of 0.05 mA/cm at a field of 0.12 MV/cm. Thus we did compare both MOS
structures to conclude that all parameters vary only because of resistance of the top electrode. Therefore, we may conclude that if ZrN has to be used in IC technologies, then the resistance of ZrN has to be minimized. However, based on our observation, ZrN could however be used in IC technology where fixed capacitors are required.

Finally, ZrN/TiO$_2$/ZrN metal-insulator-metal (MIM) device was fabricated and characterized by C-V and I-V measurements. C-V curve showed no variation in the capacitance value as the bias voltage was changed, indicating the absence of an interfacial layer between the films and electrode. I-V characteristics of the capacitor showed a very high leakage current (mA) with a very low breakdown voltage of 0.06 MV/cm. Conduction mechanisms was due to space charge limited currents which was confirmed from log I versus V^{1/2} curve.

**SCOPE OF FUTURE WORK**

Any metallization in integrated technology is improving and progressing towards a new trend i.e. use of metallization to create three-dimensional devices structures. In future, like aluminium, zirconium nitride can also be used as a top-level electrode in integrated circuit technology if by some means its resistance is lowered.

An addition of silicon into ZrN thin film can improve its decorative, corrosion resistance and hard coating property. In the same way, adding an impurity in ZrN thin films can even reduce its resistance, by increasing its conductivity, which shall surely benefit ZrN in commercial application of integrated technology.

Our study showed that DC reactive magnetron sputtering is one of the best, simpler, less time consuming techniques for depositing many ZrN films over a large scale. As we have not attempted to vary the substrate temperature either by biasing or heating, certain positive variation improvement can also be obtained in its characteristic behavior/feature as normally it does happen in bias sputtering.

Aging effect of our metal-semiconductor and metal-oxide-semiconductor structure can also be one of the future works, as any new device should be stable enough for its application purpose over a long period.
Electrical properties of all devices fabricated and characterized have been determined at room temperature. I-V and C-V measurements can also be characterized at different temperatures. This study can be an interesting area for future research.