The conventional ultraviolet (UV) photodetectors like vacuum diode, photomultiplier tubes etc are bulky devices which needs vacuum and also costly cathode targets. The modern photodetectors are based on the wide band gap semiconductor materials in which band to band transition has been occurred by the photogenerated charge carriers due to absorption of UV light. This band to band transition takes place in particular wavelength region and at higher wavelength, in visible region these detectors show negligible response. That’s why these detectors are well known as “visible-blind” UV photodetectors. The conventional UV photodetectors are not visible blind so it requires costly filters to sort out visible light and achieve sensitivity in UV region.

The verity of the materials have been used to fabricate solar blind UV photodetectors among them Zinc oxide (ZnO) has been selected as an eminent candidate as it has great environmental stability even in harsh atmosphere. ZnO thin films are known for the verity of nanostructures with verity of deposition techniques. This material is meticulously used because of its transparency in the visible region and the exceptional optical and electric properties. ZnO receives particular attention owing to being relatively non-toxic, thermally stable, and made from inexpensive raw materials. Doped nanocrystalline ZnO thin films are particularly used for tailoring the structural and optoelectronic properties of the host material. Many metallic elements like Mn, Co, Ni, N, C, Sb, Ga, Al etc have been used as dopant for sewing the properties of the ZnO. Al doped ZnO (AZO) thin films are widely used transparent conducting oxide. Good stability at high temperature and also in other ambients compared with other transparent conducting oxide (TCO) materials makes AZO films suitable for transparent optoelectronic based technological applications.

The metal-semiconductor-metal (MSM) UV photodetector is a simple device with two metallic contact electrodes over the semiconductors. These metallic contact electrodes are the most important component which helps to collect photogenerated charge carriers. The choice of the metal for contact electrode is
based upon the work function of the metal and semiconductor material used for the fabrication. Concerning with the MSM UV photodetector, a variety of MSM photodetector structures are fabricated and studied for high performance and visible blind devices. The variety of metals like Al, Ag, Au, Pt etc. have been printed or deposited on semiconductor surface in various fashion in order to collect more number of photocarriers generated in host material.

Present work encompasses synthesis and fabrication of the ZnO thin film based visible blind UV photodetector by simple cost effective spray pyrolysis technique. The Al doping is employed for the high performance UV photodetector. Further the buffer layer and different device structures with unlike metal contact electrodes have been employed to enhance the photosensing performance of the UV photodetector device. This work is distributed in seven chapters.

**Chapter-I** includes basic information about photoelectric effect and its types. External and internal photoelectric effect in case of photodetector has been discussed in brief. The general properties of photodetector that plays crucial role in the performance of photodetector have been mentioned. Also it comprises the types of UV photodetector. Basic principle and operation of MSM UV photodetector is discussed in detail. It includes detailed explanation of physical, chemical and structural properties of ZnO and Al doped ZnO. An extensive literature survey on ZnO and AZO based UV photodetector has been included. The literature survey on doped and undoped ZnO thin film based UV photodetector is tabulated in this chapter. The orientation and purpose of dissertation is stated at the end of the chapter.

**Chapter-II** deals with the theoretical background of the thin film deposition techniques with detail discussion on spray pyrolysis technique, thin film characterization techniques and UV sensing properties. This chapter mainly includes the classification of thin film deposition methods with brief theoretical
background of spray pyrolysis technique. It focuses on the theoretical background of various thin film characterization techniques like X-ray diffraction (XRD), Energy dispersive analysis by X-ray (EDAX), Raman spectroscopy study, Scanning Electron Microscopy (SEM) study, Optical Absorption spectroscopy study. It illustrates basic information about UV sensing properties like I-V characteristics, the photoswitching characteristics, responsivity of the UV detector and light intensity dependent property of the UV photodetector.

Chapter-III covers synthesis of ZnO thin films by simple and cost effective spray pyrolysis method. This chapter includes the experimental details about substrate cleaning, solution preparation, deposition of ZnO thin films on bare glass substrates. The required substrate temperature for the total decomposition of the precursor solution and formation of stable and pure phase of ZnO has been optimized in this section. The prepared ZnO thin films at various substrate temperatures have been characterized by using analysis techniques like XRD, SEM, and UV–Vis spectroscopy.

All the films exhibit hexagonal (wurtzite) crystal structure. It is observed that as the substrate temperature increases, the intensity of (0 0 2) peak increases up to 425°C and then intensity decreases for further increase in substrate temperature because of the crystal reorientation effect. The optimum substrate temperature for the deposition of crystallized ZnO thin films is 425 °C. At this temperature, the total diffusion of adsorbed atoms occurs on the substrate and atoms arrange along the preferred orientation of (0 0 2). The highest intensity of lattice plane (0 0 2) is assigned to the crystal growth with preferential orientation along c-axis. The SEM micrograph shows slight change in the surface morphology of ZnO films due to change in the substrate temperature. The transmittance and reflectance curves of the ZnO thin films for different substrate temperatures show the best visible transparency. A sharp absorption is observed in the UV region at 377 nm (~ 3.26 eV) because of the band-to-band transition. The I-V curves are linear and
Summary and conclusions

Symmetrical, indicating the good ohmic contact between the ZnO and the Ag electrodes and the film deposited at 425°C substrate temperature exhibits highest photocurrent (474 μA) than other films because at 425°C substrate temperature the film has highest crystallinity and transparency in visible region as mentioned above. The rise time, decay time and responsivity of the ZnO nanodevice at 425°C substrate temperature are 16 s, 18 s and 182 A/W respectively.

Chapter-IV includes synthesis and characterization of ZnO thin films at various solution concentrations. The concentrations of solution were varied as 0.05, 0.1, 0.15 and 0.2 M in order to obtain films of different thicknesses. The optimization of solution concentration was done by keeping the substrate temperature fixed at 425°C and other preparative parameters such as quantity of spraying solution (100 cc), nozzle-to-substrate distance (32 cm) etc at their fixed values. It is found that the intensity of (0 0 2) peak is relatively small for the films grown at 0.05M, but it increases with increasing concentration of precursor solution to 0.1M. However, the intensity decreases when ZnO is deposited at further concentrations. As the concentration of precursor solution increases from 0.05M to 0.1M, the crystallite size increases from 35 to 41 nm. The intensity of the (0 0 2) peak increases from 0.5 to 0.1 M concentrations which is may be due to the increase in thickness of the film. Surface microstructure of the films deposited on glass substrates was observed using AFM micrographs. It is clear that a dense nano-order spike type grain growth perpendicular to substrate surface occurs in the films. The root mean square (rms) roughness values of the ZnO thin films deposited at 0.1M solution concentration was 14.2 nm and this value is much lower than the films deposited at other concentrations. The film deposited at 0.2 M solution concentration indicates the ZnO films to be rough and covered with bulky grains. The observed interference effect in the T and R spectra are an evidence for mirror like reflecting films. With precursor concentration from 0.05 to 0.2 M, the band gap decreases from 3.38 eV to 3.25 eV. These results show that, change in crystallinity and difference in stoichiometry of the material induces modifications in the optical
Summary and conclusions

Band gap. All the ZnO UV photodetectors fabricated at different solution concentrations exhibited a very low dark current about 20 μA and apparent change in current (about 474 μA) was observed for the device fabricated by the 0.1M solution concentration. The response spectrum shows a full width at half maximum (FWHM) of only about 42 nm which means that the photodetector only respond to the photons with energy in this narrow region. As this ZnO based UV photodetector device is highly responsive about 182 A/W in UV region and prominently does not show photoresponse to visible region, which is credited to the wide band gap energy of ZnO so that no charge carrier is excited at low energy visible photons. This characteristic is essential for the applications in highly selective visible blind UV detector. The power law fitting for the plot of photocurrent versus illumination light intensity gives information about complex process of carrier generation, recombination and trapping along the nanostructure.

Chapter V deals with synthesis and characterization Al doped ZnO (AZO) thin films. AZO thin films having different doping percentages were prepared by using simple chemical spray pyrolysis method by keeping substrate temperature 425°C and precursor solution of 0.1 M concentration. The AZO films have been characterized by XRD, EDAX, Raman, SEM, AFM, UV-Vis spectroscopy methods. On Al doping the shift in the peak position of (002) peak towards higher diffraction angles compared with pure ZnO (34.61°) is observed and this shift in diffraction angle may be ascribed to the incorporation of Al into the ZnO crystal lattice. The Al substitutes into Zn sites, resulting in a reduction of the lattice constant from 5.178 to 5.166 Å. The TC of (0 0 2) peak decreases with increase in doping percentage, suggested that the crystal reorientation occurs due to the Al incorporation in ZnO crystal lattice. The chemical purity and their stoichiometry were tested by EDAX studies. The EDAX spectra show the presence of Zn, O and Al as the only elementary components indicates that the Al ion is substituting the Zn ion in ZnO lattice. Raman spectra of undoped and 2 at% Al doped ZnO thin film
Summary and conclusions

gives three peaks located at the wave numbers 439, 561 and 792 cm\(^{-1}\). Peak at 439 cm\(^{-1}\) corresponds to the E\(_2\) (high) mode and peak at 561 cm\(^{-1}\) corresponds to the A\(_2\) (LO) mode. An additional peak at 781 cm\(^{-1}\) is observed in 2 at% AZO film spectrum, which is due to Al doping. Al doped ZnO films show the petals like grains with uniform size distribution. The grain size decreased as the aluminum concentration increased. The root mean square (rms) roughness of the film increases with increase in Al concentration to reach maximum value 28 nm at 2 at% Al and decreases with further increase in Al concentration up to 9 nm at 4 at% Al doping. As Al doping concentration increases, the optical transmittance enhances up to 96% for the 2 at% Al doping and diminish for higher Al concentration. The capability of absorption of the AZO films is higher because of the Al concentration which enhances the number of free charge carriers. The pure ZnO based device gives 474 µA of photocurrent whereas Al doped ZnO based device shows a great enhancement in the photocurrent up to 600 µA (Al=2 at%) at 5V bias under illumination and as the doping concentration increases up to 4 at%, the photocurrent decreases up to 177 µA. AZO samples show fast photoresponse with 10 s response and 8 s recovery time with highest photoresponsivity 239 A/W at 365 nm which is much higher than in the visible range, indicating that a photodetector is highly sensitive in UV region and highly visible blind. The non-unity exponent in power law goes on decreasing as Al concentration increases, it means that on Al doping the process of electron–hole generation raises and mean while the recombination, and trapping of electrons enhances.

Chapter-VI deals with the study of effect of ZnO buffer layer on the performance of the ZnO and Al doped ZnO UV photodetector and also includes study of different device structures. In this study, ZnO and Al doped ZnO thin films were prepared by using simple chemical spray pyrolysis technique on ZnO buffer layer coated glass substrates. For the preparation of ZnO and AZO films on buffer layer, optimized preparative parameters such as substrate temperature:425°C,
solution concentration: 0.1M, Al doping concentration: 2 at%, nozzle to substrate distance 32 cm, quantity of spraying solution: 100 cc, and spray rate: 5 cc/min have been used. The structural, morphological and optical properties have been investigated by XRD, SEM, AFM and UV-Vis spectroscopy methods. The intensity of (0 0 2) diffraction peak of the ZnO and AZO samples with buffer layer has apparently sharpened up due to the insertion of ZnO buffer layer. Doping substitutes Al at the Zn sites, resulting in a reduction of the lattice parameters. This lattice shrinkage here might be caused by the smaller $\text{Al}^{3+}$ ions replacing the larger $\text{Zn}^{2+}$ ions. The TC of the AZO films is less than the ZnO suggested that the slight lattice mismatch and crystal reorientation occurs due to incorporation of Al in ZnO lattice. These results demonstrate that the buffer layer effectively enhances the growth of the ZnO along (0 0 2) peak. Thus this preferential growth of the ZnO crystal along the single (0 0 2) peak direction will provide the path for the photoelectron to flow towards the metal-semiconductor junction. The ZnO and AZO thin films with ZnO buffer layer show the dense, uniform and small grain like structure. The optical transmittance and reflectance of the films did not significantly change due to the of ZnO buffer layer due to its low thickness. It is observed that insertion of buffer layer enhances the band gap energy from 3.21 to 3.29 eV which is attributed to the change in the crystallinity and lattice parameters of the ZnO thin films. The obtained photocurrent for ZnO with buffer layer and AZO with buffer layer device respectively is 651 μA and 874 μA. The importance of the ZnO buffer in UV detection performance is that, the bonding between the buffer layer and upper ZnO layer makes good electrical contacts across the interface allows the efficient charge injection. ZnO thin film with buffer layer and AZO thin film with buffer layer based UV photodetector device shows the maximum photocurrent with higher photoresponse as compared with the pure ZnO thin film based UV photodetector. The photodetector with AZO/ZnO configuration has maximum responsivity of 340A/W, compared to the one based on ZnO/ZnO device configuration (253 A/W) and ZnO buffer layer (29 A/W). **Chapter-VI** also includes
Summary and conclusions

the comparative study of three UV photodetectors with different devices structures. The device (c) shows more dark current than other two devices because in this device FTO has been used as one contact electrode which is deposited at the base of the ZnO film and which has high conductivity at ambient conditions. The high photocurrent in case of device (c) is due to the photoresponse of SnO$_2$ also. Device (b) shows comparatively less photocurrent amongst all. The device (c) shows the rise time to be 16 s and the decay time of 23 s. For the device (b), the light rise and decay time is 14 s and 18 s, smaller than that of the device (c). The device (a) exhibits shorter response and decay time 12 s and 9 s respectively which is faster in comparison to that of the device (b) and device (c), this can be attributed to the faster carrier transport process resulted from much higher carrier concentration at the metal-semiconductor interface. The device (a), (b) and (c) shows responsivity of 102, 181 and 205 A/W respectively.

From this study it is concluded that the Al doped ZnO with ZnO buffer layer (AZO/ZnO) UV photodetector device with two Ag electrodes printed on surface gives higher UV performance. Device shows rise and decay time to be 12 s and 9 s respectively which are faster amongst other. Also AZO/ZnO device shows maximum responsivity of 340A/W in UV visible region and almost negligible in visible region. All these observations suggest the AZO/ZnO is a prominent candidate for “visible-blind” UV photodetector.