6.1 Introduction

In ZnO UV photodetector, contact electrodes are formed by different metals having different barrier heights, which significantly affect on the performance of the UV photodetector. To produce high-performance MSM UV photodiodes, it is important to achieve a barrier height at the metal–semiconductor interface that leads to small leakage current and high breakdown voltage which could result in improving responsivity and photocurrent to dark current contrast ratio. To achieve such barrier height on ZnO, one can choose metals with proper work functions [1].

In this chapter, synthesis and fabrication of the solar blind UV photodetector based on ZnO and Al doped ZnO (AZO) thin films grown on the ZnO buffer layer coated on glass substrate by spray pyrolysis method are reported. The effect of buffer layer on the physicochemical and UV photodetector properties of two different device combinations is discussed at length. The study clearly shows that, due to the insertion of ZnO buffer layer, ZnO based UV photodetector show maximum photoresponse and higher spectral responsivity in UV-A region. Further we have studied different device structures using different metal contact electrodes and test the UV performance of the devices.

6.2 Experimental details

6.2.1 Substrate cleaning process

The substrate cleaning process discussed in section 3.2.1.1 was used.

6.2.2 Synthesis of undoped and Al doped ZnO thin films grown on ZnO buffer layer

Materials: commercially available zinc acetate dihydrate (Zn(CH$_3$COO)$_2$·2H$_2$O) and aluminum nitrate (Al(NO)$_3$·9H$_2$O) were used as received.

Synthesis process: 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. Other synthesis details have discussed in the section no.
3.2.2 and 5.2.2 for ZnO and AZO films respectively. ZnO buffer layer was deposited on glass substrate by spray pyrolysis method. For the preparation of ZnO and AZO films on buffer layer we have used 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.

### 6.2.3 Characterization techniques

The prepared ZnO thin films have characterized using different analysis techniques. The details about the techniques and instrumentation have been discussed briefly in section 3.2.3.

Device testing: Photoconductive ZnO and AZO based UV detector devices [1 cm × 1 cm] in metal–semiconductor–metal (MSM) configuration was fabricated. The Ag contacts have drawn on the film surface worked as metal contact electrodes.

![Fig. 6.1 The schematic of the (a) ZnO and (b) AZO thin film device](image)

The schematic of the ZnO and AZO thin film devices with ZnO buffer layer are shown in Fig. 6.1.

### 6.3 Results and discussion

#### 6.3.1 Structural analysis

Fig. 6.2 shows XRD patterns of the samples: ZnO buffer layer, ZnO thin film with ZnO buffer layer and AZO with ZnO buffer layer. These XRD patterns are in good agreement with the standard diffraction data (JCPDS card no. 01-075-0576) and all samples exhibited hexagonal wurtzite crystal structure. It is observed that,
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. Along with this, other less intense peaks indexed as (1 0 0), (1 0 1), (1 0 2), (1 1 0), (1 0 3), and (1 1 2) are also observed. It is also observed from the XRD pattern that Al doping widens the peak width and lowers the intensity of the peaks. This increase in full width at half-maximum (FWHM) and decrease in intensities are attributed to the smaller grain size and the deteriorated crystallinity.

![X-ray diffraction patterns](image)

**Fig. 6.2 X-ray diffraction patterns for (a) ZnO buffer layer, (b) AZO with buffer layer and (c) ZnO with buffer layer**

Doping substitutes Al at the Zn sites, resulting in a reduction of the lattice parameters. Lattice parameters are calculated by the formula

\[
\frac{1}{d^2} = \frac{h^2 + hk + k^2}{a^2} + \frac{l^2}{c^2}
\]

and are summarized in Table 6.1. Due to Al doping Lattice parameter ‘c’ reduces from 5.1752 to 5.0708 Å. This lattice shrinkage here might be caused by the smaller Al\(^{3+}\) ions (ionic radius of 0.53 Å) replacing the larger Zn\(^{2+}\) ions (ionic radius of 0.74 Å) [2]. The average crystallite size ‘D’ was calculated using Scherrer
equation 2.2. Table 6.1 gives the crystallite size of the deposited films. The preferred orientation of the AZO thin films has been evaluated by calculating texture coefficient (TC) using the equation 2.4

In Table 6.1, variation of texture coefficient in (0 0 2) peak has been shown. The TC of (0 0 2) reflection of the ZnO and AZO film with buffer layer increases, suggested that the preferential crystal growth along (0 0 2) peak occurs due to ZnO buffer layer. 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.

**Table 6.1 Values of various parameters calculated from XRD pattern, AFM images and optical absorption spectra**

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Device</th>
<th>ZnO Buffer layer</th>
<th>ZnO with Buffer layer</th>
<th>Al:ZnO with Buffer layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystallite size (nm)</td>
<td>44</td>
<td>42</td>
<td>34</td>
<td></td>
</tr>
<tr>
<td>a (Å)</td>
<td>3.2441</td>
<td>3.2589</td>
<td>3.2379</td>
<td></td>
</tr>
<tr>
<td>c (Å)</td>
<td>5.2462</td>
<td>5.1752</td>
<td>5.1663</td>
<td></td>
</tr>
<tr>
<td>TC of (0 0 2)</td>
<td>2.5967</td>
<td>5.0537</td>
<td>4.1889</td>
<td></td>
</tr>
<tr>
<td>Roughness (nm)</td>
<td>116</td>
<td>144</td>
<td>110</td>
<td></td>
</tr>
<tr>
<td>Grain diameter (nm)</td>
<td>29</td>
<td>49</td>
<td>28</td>
<td></td>
</tr>
<tr>
<td>Band Gap (eV)</td>
<td>3.21</td>
<td>3.28</td>
<td>3.29</td>
<td></td>
</tr>
</tbody>
</table>

### 6.3.2 Morphological analysis

Fig. 6.3 shows the surface morphology of ZnO thin films with and without buffer layer and AZO thin film with buffer layer. SEM image of the ZnO buffer layer shows uniformly distributed grains. This textured morphology is a consequence of the nucleation sites that impinge vertically to glass substrate.
Surface micrographs apparently affected by the doping. But the ZnO and AZO thin films with ZnO buffer layer show the dense, uniform and small grain like structure.

Fig. 6.3 SEM images of a) ZnO buffer layer, (b) ZnO with buffer layer and (c) AZO with buffer layer.
Fig. 6.4 AFM images of (a) ZnO buffer layer, (b) ZnO with buffer layer and (c) AZO with buffer layer

The surface topography of the AZO thin films has been further assessed by atomic force microscopy (AFM). The AFM images shown in Fig. 6.4 are recorded under tapping mode over 5 μm x 5 μm scanning area. Fig. 6.4 revealed the AFM images of the ZnO buffer layer and ZnO and AZO thin films with buffer layer. The grain size and rms roughness of these films are summarized in Table: 6.1. Change in the morphology may due to the formation of nucleation sites and the change in the nucleation type from heterogeneous to homogeneous means from glass to buffer layer.

6.3.3 Optical properties

Fig. 6.5 shows the optical transmittance and reflectance spectra of the ZnO buffer layer, ZnO and AZO thin films with buffer layer. Films are highly transparent with transmittance greater than 90% for all the films over visible region (400-700 nm) and sharp absorption edge at the 375 nm wavelength is observed. Fig. 6.5 also shows the reflectance spectra of the thin films. Film thickness was estimated using observed reflectance spectra and refractive index database for ZnO single crystal. The film thickness is in the range of 200-350 nm. The optical
transmittance and reflectance of the films did not significantly change due to the of ZnO buffer layer due to its low thickness [3-4].

![Graph showing optical absorption spectra](image)

**Fig.: 6.5 Optical absorption spectra of ZnO buffer layer, ZnO with buffer layer and AZO with buffer layer. Inset shows the plot of \((ahv)^2\) Vs hv**

Fig. 6.6 shows the absorption spectra of the ZnO buffer layer, ZnO and AZO thin films with buffer layer. It is seen that the ZnO and AZO thin films with buffer layer has less absorption in the visible region. Inset of Fig. 6.6 shows the plot of \((ahv)^2\) Vs hv for the ZnO and AZO thin films with buffer layer. It is observed that insertion of buffer layer enhances the band gap energy from 3.21 to 3.29 eV. This enhancement in the optical band gap is attributed to the change in the crystallinity and lattice parameters of the ZnO thin films. AZO thin film with buffer layer has slightly higher band gap energy because of the doping. Similar type of results has also observed by Mahmood et al. and Gao et al. [5-6].
Figure: 6.6 Optical absorption spectra of ZnO buffer layer, ZnO with buffer layer and AZO with buffer layer. Inset shows the plot of $(\alpha h\nu)^2$ Vs $h\nu$

6.3.4 UV sensing properties
I-V characteristic of the UV detector

Fig. 6.1 shows the schematic of the ZnO and AZO thin film device with ZnO buffer layer MSM UV photodetector, as well as the Ag electrodes printed on top of the thin film. Fig. 6.7 show the I-V characteristic of the devices (Fig. 6.1) under dark and under UV illumination of wavelength 365 nm at fixed 5V external applied bias. At an applied bias voltage of 5V larger number photogenerated electrons can cross electrode/ZnO interface, whereas at lower applied bias voltage very few electrons could pass the interface and result in poor photoresponse. Further at relatively higher bias voltage, the band edge response extends towards visible region [7]. This visible light response upon applying a relatively higher bias voltage
is due the fact that, at higher bias voltage the more number of electrons can be injected into the surface states of ZnO.

![Graph showing I-V characteristics of UV photodetectors](image)

**Fig. 6.7 I–V characteristics of the UV photodetectors under UV illumination**

\( (\lambda=365 \text{ nm}) \)

Thus these electrons can also be filled into depletion region, resulting into a reaction of \( V_{o}^{+} \) and \( V_{o}^{++} \) to \( V_{O} \), namely trap filling and correspondingly, the potential barrier height and depletion region width will decrease [7]. The obtained photocurrent for the devices is much higher than the dark current. This I-V characteristic of the device clearly shows the ohmic contacts between the deposited film and Ag electrodes. The devices show less dark current because of high material resistivity [8] and resistivity of the fabricated device increases due to the insertion of buffer layer between glass and ZnO film. The obtained photocurrent for ZnO with buffer layer and AZO with buffer layer device respectively is 651 \( \mu A \) and 874 \( \mu A \) which is higher than that of reported UV photodetector devices with structures like glass/Ag/ZnO seed layer/ZnO nanowires [8], n-Si (111)/SiO\(_2\)/ZnO buffer layer/ZnO nanorods/Ag finger contacts [9]. 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. The photogenerated electrons inside the ZnO thin film diffuse to ZnO buffer layer along the c-axis since the upper ZnO layer are electrically floated. Thus the electrons can be effectively diffused into the ZnO buffer layer and will collect together at the ZnO upper layer/ZnO buffer layer interface, and then the two-dimensional electron gas (2DEG) will form [10]. The 2DEG will decrease the transverse resistances between the interfaces strongly [11], and then the photogenerated electrons may reach easily to Ag electrode. The consequence of the buffer layer is also revealed by the results of structural and morphological analysis.

The photoswitching characteristic of the UV detector

![Fig. 6.8 Time-resolved photocurrent of the ZnO based photodetector with UV light modulation for 30 sec at a 5 V bias voltage.](image-url)
The time dependant photocurrent under the modulated UV light illumination with wavelength 365 nm with 5 V bias demonstrated in the Fig. 6.8 indicates that the detector has good photoconductivity and repeatability. It shows the photoresponse for the ZnO buffer layer, ZnO thin film with buffer layer and AZO with buffer layer. AZO film has long tail in decay duration near to the dark current. In the response and decay time of the detector, surface oxygen exchange process plays the dominant role in the photoelectric phenomenon of the UV detector [8]. From the photoresponse curve it is clear that initially response to UV radiation is fast followed by slow process and it did not saturate upto 30 s. The photoresponse of ZnO consists of two parts. The initial fast response due to reversible solid-state processes, such as intrinsic inters band transition, and the later slow response is mainly due to the oxygen adsorption-photodesorption and defect related recombination processes [12]. The decay of the curve has also two sections it is fast initially and slows down as reaching the plateau. At the initial stage of the decay curve when UV light is turned off, the higher concentration of the oxygen vacancies on the surface of the ZnO film gives higher probability of adsorption of oxygen molecule, resulting in decrease of current. As the adsorption proceeds, the available defect sites on the surface will decrease, so extra adsorbant should diffuse deeper into the film to find out the available defect sites, requiring thermally activated diffusion energy, which slower the decay process [13]. 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 studied in section no. 3.3.5. In this device structure buffer layer play important role due to the buffer layer, the growth of the film is highly directed along c-axis along (002) peak and offered high crystalanlity to the film as shown in XRD results. This buffer layer also gives path for the electron to diffuse through the ZnO buffer layer and collect at the electrode interface.
The responsivity of the UV detector as a function of wavelength

The photodetector is also characterized by the one more performance metric “responsivity”. Responsivity (R), is the ratio of the device photocurrent (I_p) to the incident optical power (P_opt) given in equation no. 1.6. Fig. 6.9 shows the spectral responsivity of the ZnO buffer layer, ZnO/ZnO and AZO/ZnO UV photodetector.

From the curves of the responsivity of the photodetector, it can be noted that the MSM photodetector exhibited spectral response mainly over the range 325 to 375 nm and drops drastically across the wavelength 375 nm which nearly close to the sharp absorption edge observed in the transmittance spectra of the ZnO, confirming that this to be a band to band transition. At the wavelength above 375 nm, the photodetector shows little responsivity, and the responsivity decreases with the increase in wavelength. This shows that the photodetector have high responsivity for solar blind light with less influence of visible light.

![Responsivity vs Wavelength](image)

**Fig. 6.9** The spectral response of the photocurrent measurement of ZnO based MSM photodetector
The photodetector with AZO/ZnO configuration has maximum responsivity of 340 A/W, compared to the one based on ZnO/ZnO device configuration (253 A/W) and ZnO buffer layer (29 A/W). It is seen that after insertion of the ZnO buffer layer device shows drastic increase in spectral responsivity. Upon UV illumination, the electrons in upper layer (deposited on buffer layer) are excited. Bonding between upper layer and buffer layer makes good electrical contact across the interface and this allows efficient charge injection. So that these excited electrons are transferred through ZnO buffer layer and then collect at metal-semiconductor junction between ZnO layer and Ag electrode, resulting in higher photoconductivity. Zhou et. al. have studied the effect of ZnO and MgZnO seed layer on the performance of the ZnO based UV photodetector and observed 0.22 A/W responsivity for photodetector with ZnO seed layer and 0.44 A/W for photodetector with MgZnO seed layer [14].

**The light intensity dependent property of the UV detector**

![Graph showing dependence of photocurrent on power density](image)

**Fig. 6.10** Dependence of photocurrent with optical power density of the ZnO photoconductive detectors at 5 V bias
The relation between photocurrent and incident power density have been shown in Fig. 6.10. The photocurrent of the device decreases noticeably with decrease in intensity of the incident light. The photocurrent, $I_{pc}$, follows a power-law relationship with intensity $P : I_{pc} \propto P^\theta$, where $\theta$ determines the photocurrent response to light intensity [15] as shown in Fig.6.11.

Table: 6.2 The variation in the non-integer exponent ‘‘$\theta$’’ of the various devices

<table>
<thead>
<tr>
<th>Device configuration</th>
<th>Exponent of in light intensity $P$</th>
<th>Power low relation</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO buffer layer</td>
<td>0.28</td>
<td>$I = P^{0.28}$</td>
</tr>
<tr>
<td>ZnO/ZnO</td>
<td>0.13</td>
<td>$I = P^{0.13}$</td>
</tr>
<tr>
<td>AZO/ZnO</td>
<td>0.12</td>
<td>$I = P^{0.12}$</td>
</tr>
</tbody>
</table>

The fitting gives non unity exponent suggests a complex process of electron–hole generation, recombination, and trapping within a semiconductor [16]. It may also be possible that the variation in the non-integer exponent ‘‘$\theta$’’ (Table 2) of the devices fabricated at AZO/ZnO and ZnO/ZnO configurations is due to the efficient charge injection at the interface between upper layer (AZO and/or ZnO) and ZnO buffer layer, recombination speed and trapping levels in the devices etc. It is seen from Fig. 6.11 that, at higher light intensity, photocurrent shows linear response to the incident light and at lower intensity it shows non linear behavior. This linear behavior at higher light intensity may be caused by electron trapping saturation and/or limitation of hole mobility in the layers of ZnO [17]. The non ideal morphology of the AZO/ZnO or ZnO/ZnO device may increase the lowest light intensity detection by the photodetector [17].
6.4 Different device structures

6.4.1 Different device structures of MSM UV photodetectors

Three different device structures namely (a), (b) and (c) have been fabricated and its comparative study is discussed in this section.

Device structures and there fabrication processes

a) Two Ag electrodes on the ZnO thin film surface as contact electrodes

The device fabrication process and schematic of the device is given in section 3.2 and Fig. 3.1 respectively.

b) Al interdigital electrodes (ITDs) on the ZnO thin film surface as contact electrodes

Al ITDs were first deposited on the bare glass substrate with thickness 40nm, and width 2mm by chemical vapor deposition technique. Al foil is
used as source for the Al ITD deposition. The photograph of the Al ITDs on bare glass substrate is shown in Fig. 6.12 (a) below. Then ZnO is coated on the Al ITDs. The device structure is shown in Fig. 6.12 (b).

![Al ITDs on bare glass substrate](image1.png)

**Fig. 6.12** Al threads (2mm width) were deposited by chemical vapor deposition technique on the bare glass substrate as contact electrodes.

c) FTO is used as one contact electrode and screen printed Ag as another contact electrode in MSM UV photodetector.

The thin layer of florine doped tin oxide (FTO) has been deposited on the bare glass. The ZnO thin film is deposited over the FTO by spray pyrolysis technique. Masking has done during the spray deposition for the contact purpose. The schematic of the device is shown in Fig. 6.13 below.

![Device schematic](image2.png)

**Fig. 6.13** FTO is a base electrode and Ag electrode printed on ZnO surface as another contact electrode.
6.4.2 UV sensing properties of the devices

I–V characteristic of the UV detector

Fig. 6.14 shows comparative current-voltage characteristics of the three devices with different structures. I-V curve clearly shows the linear current–voltage behavior indicates ohmic nature of the metal-semiconductor interface which has been discussed in earlier section. From Fig.6.14 it is assured that 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. Again under illumination device (c) shows maximum current in comparison with other devices. Hu et al [18] had recently reported SnO$_2$ based UV photodetector and resulted photodetector exhibited excellent light selectivity and stability. So this high current in case of device (c) is may be due to the photoresponse of SnO$_2$ as well. Device (b) shows comparatively less photocurrent amongst all. The

**Fig. 6.14 I–V characteristics of the UV photodetectors under UV illumination**

($\lambda=365$ nm)
first reason is the large difference in the work function of the ZnO and Al as compared with ZnO and Ag. Al has work function 4.08 eV and ZnO is having 4.95 eV. It is seen that due to the difference in the length of the two Al electrodes, the asymmetric electric potential distribution in the ZnO film could induce the difference in the carrier separation and transport. Thus, the numbers of accumulated and trapped holes at the two interfaces are different, which induces the difference in the barrier height between two Al-ZnO contact electrodes. This difference in barrier between two Al-ZnO interfaces significantly reduces the resultant photocurrent of the device.

The photoswitching characteristic of the UV detectors

Fig. 6.15 present the on-off switching characteristics (at a bias of 5V) of photoconductors based on the three different device structures. The ON and OFF time durations are both 30 seconds for all the three devices. It is clearly seen that all the devices can be switched on and off repeatedly.

![Fig. 6.15 Time-resolved photocurrent of the ZnO based photodetector with UV light modulation for 30 sec at a 5 V bias voltage](image)
Fig. 6.15 also presents the light rise and decay time information (at a bias of 5 V) of the photodetectors based on the different contact electrodes. The rise and decay time of these devices have been calculated. The device (c), shows the rise time of about 16 s and the decay time is 23 s. The photocurrent of the device mainly comes from photo-excitation dissociation from FTO induced by the applied external electric field and trapping states in the ZnO thin film [19]. Owing to the fact that carrier trapping/detrapping process needs a long time, therefore the rise and decay times is large for the device (c). 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 times of 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. This higher concentration of charge carrier is due to less difference in the work functions between metal used for contact electrode and semiconductor for the fabrication of the device.

**The responsivity of the UV detector as function of wavelength**

In order to further investigate the spectral response of ZnO based devices we calculated wavelength dependant responsivity $R(\lambda)$ using equation 1.4. The device (a), (b) and (c) shows responsivity of 102, 181 and 205 A/W respectively as shown in Fig. 6.16. The responsivity of device (c) is significantly higher for the wavelength range 350–375 nm as compared with other but it also shows substantial photoresponse in visible region above 375 nm wavelength. This photoresponse in higher wavelength region is due to the room temperature conductivity of the base electrode FTO. This observation tells that the device (c) is not visible blind and not a proper structure for the use of solar blind UV photodetector.
Fig. 6.16 Time-resolved photocurrent of the ZnO based photodetector with UV light modulation for 30 sec at a 5 V bias voltage
References


Study on effect of ZnO buffer layer and device structure on the performance of the ZnO and Al doped ZnO UV photodetector


