6. **Nanopatterned-Si surfaces: Templates for growth of Al-doped ZnO (AZO)**

Our experimental studies on potential of nanopatterned Si as templates for growth of thin films with improved properties is described in the present chapter. Aluminium-doped ZnO (AZO) films were grown on ripple and nanofaceted-Si templates using magnetron sputtering. While the AZO films grown on rippled-Si show modification in photoluminescence (PL), the AZO films on nanofactated-Si show antireflection and photovoltaic properties which are tunable through facet dimension.

6.1 Growth of AZO on rippled-Si

6.1.1 Introduction

Over the last two decades, zinc oxide has been thoroughly investigated in different industrial areas such as opto- and nano-electronics, ceramics, and photovoltaics [1,2]. Doping of Group III elements, and in particular Al, enhances the conductivity and makes it behave like a transparent conducting oxide (TCO) material. The TCOs are becoming increasingly important to improve the quality as well as efficiency of display panel and solar energy conversion devices [3]. In addition, ultra-violet (UV) light emitting diode based on ZnO are being applied in UV curing, counterfeit detection, and medical instrumentation [4] due to their outstanding properties, viz. wide band gap (3.37 eV at room temperature), high absorption in the UV range, and higher excitonic binding energy (60 meV) [5], compared to other materials having similar applications (e.g. GaN having an excitonic binding energy of 28 meV) [6].

Nowadays, ZnO related research for optoelectronics is growing and is focused on
improving the ZnO excitonic emission in the blue-UV region, taking advantages of its high excitonic binding energy and efficient radiative recombination even at room temperature (RT) [7,8]. Photoluminescence (PL) in the UV region is caused by free electron-hole recombination phenomena in the near band-edge. In the visible region, PL is due to the presence of chemical and structural defects such as oxygen and zinc vacancies and oxygen and zinc interstitials [9]. Free excitons are bound electron-hole pairs that can move together through the crystal\textsuperscript{10} and are useful in optoelectronics and photovoltaics [11-13]. On the other hand, materials having excitons bound to structural defects can be used as laser media [14,15]. Different reports exist showing a dependence of excitonic energy on the dimension of ZnO nano-objects [16,17]. One of these reports indicates confinement effects in polycrystalline ZnO-based films with grain size as the confined dimension [19]. Thus, tailoring the optical properties by varying structure, size, and composition of a material is of utmost importance.

As an alternative, optical properties can also be tuned by using a template for deposition of thin films where self-organized substrates lead to conformal growth [20-22]. Recently, the efficacy of low energy ion-beam fabricated self-organized nanoscale ripple-patterned substrates has been demonstrated as templates to grow Ag nanoparticle arrays [20,22,23]. We have studied the conformal growth of Al-doped ZnO (AZO) overlayers on ion-beam synthesized nanofaceted-Si templates, leading to tunable antireflection property for improved solar cell performance [24]. In that case, height of the nanofacets was comparable to the wavelength of incident light. On the other hand, the vertical dimension of low energy ion-beam induced ripples (i.e. ripple amplitude) are orders of magnitude smaller compared to light wavelengths and hence, the growth of AZO overlayers on rippled-Si substrates should manifest very different optical properties. Thus, understanding the role of anisotropic rippled-Si templates in achieving size-dependent optical properties of AZO nanostructured thin films will be of importance for potential applications in nanophotonics.
In this paper, we report on growth of self-organized AZO thin films on rippled-Si templates to address morphological anisotropy-driven thickness-dependent tuning of their optical properties. As a comparative study, we also present our experimental results on AZO overlayers of same thicknesses simultaneously grown on pristine-Si substrates. Atomic force microscopy (AFM)-based morphological studies reveal the signature of conformal growth, giving rise to chain-like structures of AZO on rippled-Si templates (up to a thickness of 15 nm). On the other hand, growth of only granular AZO overlayers is observed on pristine-Si substrates. Photoluminescence (PL) study was performed at RT on both type of substrates to study thickness-dependent excitonic response. For instance, 10-nm thick AZO film grown on rippled-Si shows a blue shift (6 nm) in the free excitonic peak (with respect to the same thickness grown on pristine-Si) which diminishes with increasing film thickness. The observed thickness-dependent blue shift is attributed to quantum confinement effect, originating from the AZO grain size and their spatial arrangement governed by underlying substrates having morphological anisotropy.

6.1.2 Experimental

For fabrication of rippled-Si templates, a p-type Si(100) wafer was sliced into small pieces (1 cm×1 cm) and these pieces were exposed to 500 eV Ar+-ions at an oblique incidence of 63° (with respect to the substrate surface normal). A fixed ion fluence of 5×10\(^{17}\) ions cm\(^{-2}\) was used corresponding to the ion flux of 1.3×10\(^{14}\) ions cm\(^{-2}\) s\(^{-1}\). Details of the experimental geometry is described elsewhere [25]. The ion-exposed substrates were subsequently transferred to a deposition chamber for growth of AZO films by using pulsed dc magnetron sputtering technique. Commercially available 99.99% pure (Testbourne, UK) ZnO:Al\(_2\)O\(_3\) (2 wt.%) target (5.08 cm diameter and 0.64 cm thick) was used for growth of AZO overlayers in a vacuum chamber with a base pressure of 3×10\(^{-7}\) mbar. Ultra-pure (99.999%) argon gas was injected into the chamber with a flow rate of 30 sccm to maintain a working pressure of 5×10\(^{-3}\) mbar.
during sputtering. A pulsed dc power of 100 W (frequency = 150 kHz and reverse time = 0.4 μs) was supplied (Advanced Energy, Pinnacle Plus) to the AZO target where the target-to-substrate distance was fixed at 10 cm. The deposition was carried out at an optimized angle of 50° with respect to the target normal [26]. Two sets of AZO films having thicknesses of 10, 15, and 30 nm were deposited simultaneously on pristine- (named as P1, P2, and P3, respectively) and rippled-Si (named as R1, R2, and R3, respectively) substrates with an average deposition rate of 5 nm min⁻¹. For AZO growth on rippled-Si templates, projection of the incoming flux was ascertained to be parallel to the direction of the ripple wave-vector (Fig. 6.1). The corresponding thicknesses were measured by using a surface profilometer (Ambios, XP-200).

Figure 6.1 Schematic of the ion-beam fabrication of rippled-Si and its further usage as a template for growth of AZO films. The projection of incoming flux during deposition was kept same as that of the ion-beam projection onto pristine-Si surface for fabrication of ripples.

Phase identification and crystalline orientation were investigated by x-ray diffraction (XRD) (Bruker, D8 Advance) measurements, using a Cu-Kα radiation (λ=0.154 nm) over a 2θ scan range of 20°–60°. Surface morphology was examined by ex-situ atomic force microscopy (Asylum Research, MFP3D) in tapping mode. For each sample, several images were taken from different regions to check the uniformity and to estimate the average grain size and root mean square (rms) roughness. AFM images were analyzed by using WSxM and Gwyddion softwares [27,28]. Cross sectional transmission electron microscopy (field emission gun based 300 keV
FEI Tecnai G2 S-Twin) studies were performed on selective samples for microstructural analysis. Optical properties of the deposited films were studied by using a photoluminescence spectrometer (Perkin Elmer, LS-55), having a Xe-lamp with excitation wavelength of 325 nm at RT. The compositional analyses of AZO overlayers were carried out by using x-ray photoelectron spectroscopy (VG Instrument).

6.1.3 Results and discussion

Figures 6.2(a)-(h) show AFM micrographs of rippled- and pristine-Si substrates before and after the growth of AZO overlayers of different thicknesses, viz. 10 nm, 15 nm, and 30 nm. Profilometric measurements show that the films are highly uniform in thickness (within 1 nm). From Fig. 6.2(a), we observe that the ripples have wavelength of 28±1 nm and amplitude of 3 nm. Figures 6.2(b)-(d) depict the morphologies of R1, R2, R3 where corresponding two-dimensional (2D) fast Fourier transforms (FFT) are shown in the insets. These clearly illustrate the presence of anisotropy in the x-direction up to an AZO thickness of 15 nm. It may be pointed out that in Figs. 6.2(b) and (c), signature of the rippled templates after AZO growth is still visible. Thus, we can infer that the film morphologies have a bearing on the underlying ripple morphology up to the thickness of 15 nm and beyond that a granular morphology evolves [Fig. 6.2(d)]. On the other hand, films deposited on pristine-Si [Figs. 6.2(f)-(h)] substrates show only isotropic growth (as confirmed from 2D FFTs presented as insets on the respective AFM images) having granular morphologies.
Figure 6.2: AFM images: (a) rippled-Si, (b) R1, (c) R2, (d) R3, (e) pristine-Si, (f) P1, (g) P2, and (h) P3. Insets are 2D FFT of the respective images. The white arrow in (a) indicates the projection of argon ion-beam onto the pristine-Si substrate. The height scales in (a)-(h) are: 6 nm, 9 nm, 10 nm, 12 nm, 1 nm, 6 nm, 8 nm, and 9 nm, respectively.

Various parameters, extracted from the AFM images, are summarized in Table 6.1. It is observed that rms roughness increases with thickness for films grown on both pristine- and rippled-Si substrates.
Table 6.1: Various parameters extracted from AFM analyses

<table>
<thead>
<tr>
<th>Sample</th>
<th>rms roughness (nm)</th>
<th>Wavelength (nm)</th>
<th>Av. Grain size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rippled-Si</td>
<td>0.76</td>
<td>28 ± 1</td>
<td>--</td>
</tr>
<tr>
<td>Pristine-Si</td>
<td>0.098</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>R1</td>
<td>1.10</td>
<td>28 ± 1</td>
<td>15±2</td>
</tr>
<tr>
<td>P1</td>
<td>0.60</td>
<td>--</td>
<td>20±2</td>
</tr>
<tr>
<td>R2</td>
<td>1.124</td>
<td>28 ± 1</td>
<td>25±2</td>
</tr>
<tr>
<td>P2</td>
<td>0.64</td>
<td>--</td>
<td>27±2</td>
</tr>
<tr>
<td>R3</td>
<td>1.39</td>
<td>--</td>
<td>28±2</td>
</tr>
<tr>
<td>P3</td>
<td>1.03</td>
<td>--</td>
<td>30±2</td>
</tr>
</tbody>
</table>

Figure 6.3 shows XRD patterns obtained from samples R3 and P3 where the (002) reflection corresponding to hexagonal wurtzite structure is observed, implying the films are preferentially oriented along the $c$-axis. It may be mentioned that for lower film thicknesses (<30 nm), XRD signals were not strong enough and hence, corresponding microstructural analyses of those films were carried out using cross-sectional transmission electron microscopy (XTEM) in a selective manner.

Figure 6.3: XRD spectra corresponding to 30 nm-thick AZO overlayers: R3 and P3.
Figure 6.4 presents XTEM data corresponding to the sample R2. The undulated nature (with wavelength of 28.8 nm) of the interface is evident from this XTEM image. Figure 6.4(a) reveals that the AZO overlayer of 15.9 nm thickness grows conformally (indicated by dashed yellow line) on the rippled-Si substrate covered with a thin native oxide layer. In addition, the columnar growth of AZO overlayer is obvious from this image [Fig. 6.4(b)] [26]. The presence of lattice fringes in the high-resolution TEM (HRTEM) image [Fig. 6.4(b)] indicates the high quality of the conformally grown AZO film. The calculated $d$-spacing from the zoomed portion of the HRTEM image [Fig. 6.4(c)] turns out to be 0.26 nm which matches well with the $d_{002}$ of wurtzite ZnO [29]. Thus, the XTEM data corroborates well with our XRD data corresponding to 30 nm-thick films described above.

Figure 6.4: (a)-(c) present XTEM micrographs corresponding to R2: (a) Low-magnification image, showing a uniform and conformal growth of AZO on the native oxide covered rippled-Si substrate, (b) HRTEM image obtained from the marked region on (a), showing the interface regions of native oxide covered rippled-Si substrate and AZO overlayer, where columnar growth of AZO film is demonstrated by dashed yellow lines on the same. (c) HRTEM image taken from the marked region on (b), which shows lattice fringes.
Compositional analyses of AZO films were carried out by x-ray photoelectron spectroscopy (XPS) measurements. The survey spectra (not shown) of all samples do not reveal the presence of any undesirable species (impurity). Figures 6.5(a)-(d) depict Zn 2p and O 1s core level spectra corresponding to two AZO films deposited on rippled-Si. In particular, Figs. 6.5(a) and (b) correspond to sample R1 while 6.5(c) and (d) represent R2. In order to maintain the clarity, we have not presented the XPS spectra corresponding to the sample R3. Details of the XPS analyses for all AZO films deposited on rippled-Si substrates are summarized in Table 6.2. It is observed that XPS spectra of the Zn 2p3/2 and Zn 2p1/2 levels are nearly centered at binding energy values of around 1021.4 eV and 1044.5 eV, respectively, corresponding to Zn atoms at regular sites of an AZO lattice. The difference in the binding energies of Zn 2p3/2 and Zn 2p1/2 is found to be 23.1 eV, which is a characteristic value of AZO [30,31]. On the other hand, individual O1s peak is deconvoluted to have three distinct curves centered at binding energies around 530, 531.4, and 532.1 eV. The lowest binding energy curve at 530 eV is attributed to O atoms at regular lattice site (O_L). In other words, the intensity of this peak is a measure of the amount of oxygen atoms in a fully oxidized stoichiometric surrounding [30,32]. The intermediate binding energy of 531.4 eV is associated with O atoms in the oxygen deficient regions (O_v) within the AZO matrix and the peak corresponding to the binding energy of 532.1 eV is attributed to the presence of interstitial O atoms (O_i) or non-stoichiometric oxygen, belonging to either of the species such as adsorbed H_2O or O_2 on the surface of AZO films [30,32].
Figure 6.5: Core-level Zn2$p$ and O1$s$ spectra of AZO films having thicknesses of 10 nm [(a)-(b)] and 15 nm [(c)-(d)] grown on rippled-Si templates.

It is observed from Table 6.2 that, with increasing AZO thickness, the concentration of interstitial O (O$_i$) increases and reaches its maximum (63.23%) for the 30 nm-thick film. On the other hand, the concentration of O$_v$ shows a random behaviour for film thickness greater than 15 nm, although its origin is not clear to us at this point. It may be mentioned that XPS analyses of samples P1, P2, and P3 (which show granular morphologies) yield similar results and hence, are not presented here. Another crucial observation is that simultaneously the concentration of regular oxygen atoms at regular lattice sites reduces from 56.27% to 20.41% as a function of AZO film thickness.
Table 6.2: Results of XPS analyses for AZO films grown on rippled-Si templates

<table>
<thead>
<tr>
<th>Sample</th>
<th>Binding energy (eV)</th>
<th>Composition</th>
<th>Relative percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1 (O1s)</td>
<td>529.9</td>
<td>O1s, O_L</td>
<td>56.27</td>
</tr>
<tr>
<td></td>
<td>531.4</td>
<td>O1s, O_v</td>
<td>23.92</td>
</tr>
<tr>
<td></td>
<td>532.2</td>
<td>O1s, O_i</td>
<td>19.81</td>
</tr>
<tr>
<td>R2 (O1s)</td>
<td>530.03</td>
<td>O1s, O_L</td>
<td>33.80</td>
</tr>
<tr>
<td></td>
<td>531.53</td>
<td>O1s, O_v</td>
<td>27.41</td>
</tr>
<tr>
<td></td>
<td>532.11</td>
<td>O1s, O_i</td>
<td>38.79</td>
</tr>
<tr>
<td>R3 (O1s)</td>
<td>530.05</td>
<td>O1s, O_L</td>
<td>20.41</td>
</tr>
<tr>
<td></td>
<td>531.5</td>
<td>O1s, O_v</td>
<td>16.36</td>
</tr>
<tr>
<td></td>
<td>532.1</td>
<td>O1s, O_i</td>
<td>63.23</td>
</tr>
</tbody>
</table>

PL spectra collected at RT for films deposited on both pristine- and rippled-Si templates are shown in Fig. 6.6. All the samples exhibit complex PL spectra with several bands, covering both UV and visible ranges (350-500 nm). The peak in the UV region corresponds to the free excitonic emission, which is also referred to as the near band-edge emission. This excitonic peak is located around 376 nm in all AZO films deposited on pristine-Si substrates. It is observed that for both type of substrates, intensity of the excitonic peak reduces with increasing film thickness and a broad band in the visible region starts dominating for the whole spectra (corresponding to the highest thickness of 30 nm). It is generally accepted that the signal in the visible range arises from excitons that are bound to acceptor and donor defects (bound excitons) [33,34]. As a matter of fact, these bound excitons are trapped by the intrinsic defects in the films which correspond to various energy states for deep level emission. This corroborates well with our XPS studies, confirming the presence of defects like O_v and O_i which are known to cause emission in the visible region [35].

It is well-known that ZnO is a polar compound and hence, its thin polar films [36-38] can easily adsorb radical species. The XPS results support this polarity effect in case of AZO films.
Figure 6.6: PL spectra of AZO films recorded at room temperature: (a) 10 nm, (b) 15 nm, and (c) 30 nm-thick films on pristine- and rippled-Si substrates.

as well, since adsorbed OH species are identified from the O1s (at around 532.1 eV binding energy) spectra. The free excitonic emission is known to be suppressed in the presence of these adsorbed species [39]. Thus, reduction in the intensity of the excitonic emission line, with
increasing AZO thickness, can be attributed to the higher amount of adsorbed radical species at the surface of AZO films.

Another key observation from our PL studies is the blue shift in case of AZO samples deposited on rippled-Si substrates (viz. R1 and R2) with respect to those of similar thicknesses deposited on pristine-Si substrates (viz. P1 and P2). For instance, R1 shows the maximum shift of 6 nm with respect to its counterpart, P1. On the other hand, for R2, the excitonic peak shift reduces to 3 nm (with respect to P2), whereas R3 shows hardly any blue shift.

In order to understand such a PL behaviour in case of R1, R2, and R3 (compared to P1, P2, and P3, respectively), we have presented the AFM phase contrast image of sample R1 in the inset of Fig. 6.7. It is known that, in general, an AFM phase image gives a better resolution [40] and it is possible to detect very small features which may otherwise remain hidden in the normal topographic images. A careful observation of the inset in Fig. 6.7 reveals that bigger grains of R1 are comprised of very small grains (marked by green peripheral lines) having an average size of~15 nm and they are arranged conformally with respect to the underlying rippled-Si substrate. However, this conformal nature of AZO grains disappears for 30 nm-thick film (as discussed earlier).

In a recent paper, Nie et al. mentioned that due to the quantum confinement effect, smaller mean grain size of films leads to increased excitonic peak energy [19]. The present experimental results indicate that not only the size of the grains are important to cause confinement of the free excitons, but also their spatial arrangement is equally important. According to Nie et al., the band gap energy of the confined nanostructures can be expressed as $E_g(eV) = E_{g,\text{bulk}} + A/D^2$, where $E_{g,\text{bulk}}$ is the band gap for the bulk material, $A$ is the quantum confinement constant, and $D$ is the grain size. Here we consider, $E_{g,\text{bulk}} = 3.37$ eV, $A = 6.8$, and $D = 15$ nm (corresponding to R1) [19]. Putting these values in the above expression, one obtains $E_g$ to be 3.4 eV which is very close to the value corresponding to the excitonic peak appearing
at 370 nm (or 3.35 eV) for R1. On the other hand, for R2, the average grain size turns out to be 25 nm. Thus, using the above relation, $E_g$ turns out to be 3.38 eV, whereas the experimental excitonic peak appears at 3.33 eV. These calculations demonstrate a probable free excitonic confinement in case of chain-like AZO structures grown anisotropically on rippled-Si. In contrast, for a 30 nm-thick AZO film grown on rippled-Si (i.e. R3), albeit the average grain size is ~28 nm, we do not see any aligned chain-like features as well as any meaningful blue shift of the excitonic peak ($E_g=3.37$ eV). This may be attributed to the fact that this value is greater than the upper limit of the critical grain size up to which quantum confinement effect was observed for ZnO [19].

Figure 6.7: Variations in free excitonic shift and average grain size of R1, R2, and R3 as a function of thickness. The inset shows AFM phase contrast image of R1, where the presence of smaller grains are evident (marked by green closed loops). The range of the scale bar in this case is -3° to +12°. The solid lines are guide to the eyes.

Fig. 6.7 presents the variations in the excitonic peak shift and the average grain size (for AZO films grown on rippled-Si templates) as a function of AZO thickness, which show opposite
trends. Although there is a slight mismatch between the experimental and theoretically calculated values of $E_g$ for R1, R2, and R3, the observed trend in blue shift matches well with Fig. 6.7. It may be mentioned that for all AZO films grown on pristine-Si substrates (i.e. P1, P2, and P3), the excitonic peak appears at 376 nm (or 3.297 eV), indicating the absence of any blue shift for these granular films (showing an isotropic morphology). For instance, for a 10 nm-thick AZO film grown on pristine-Si (i.e. P1), the average grain size turns out to be ~20 nm but still no blue shift is observed (with respect to P2) [Figs. 6.6(a) and (b)]. Further, no PL signal is observed from as-prepared rippled-Si substrates as well. Thus, our investigations suggest that the undulated Si substrates underneath, having morphological anisotropy, help excitons to get spatially confined by forming chain-like structures.

6.1.4 Conclusions

In summary, we have shown the use of self-organized nanoscale rippled-Si substrates as a potential template to grow AZO thin films and modify their thickness-dependent optical properties. Free excitonic emission of AZO thin films, deposited by pulsed dc magnetron sputtering, with varying thicknesses (10, 15, and 30 nm), is investigated for pristine- and rippled-Si substrates. Films deposited on pristine-Si substrates are granular in nature, whereas AZO films of thicknesses 10 and 15 nm, grown on rippled-Si substrates, give rise to the formation of self-organized chain-like structures. On the other hand, for 30 nm-thick film grown on rippled-Si template, the chain-like morphology disappears and instead a randomly arranged granular morphology evolves. Further, 10 and 15 nm-thick AZO overlayers on rippled-Si, show blue shift in the excitonic peak which is attributed to quantum confinement effect and spatial arrangement of AZO grains driven by the morphology of the underlying rippled-Si templates. The observed trend of shift in the position of the free excitonic peak matches well with the theoretical calculations by taking into account the quantum confinement effect. It is also concluded that due to the polar nature of AZO, the absorbed species like H$_2$O
and OH on the surface of the AZO samples suppress the free excitonic emission with increasing film thickness.

6.2 Growth of AZO on nanofaceted Si

6.2.1 Tunable antireflection from conformal Al-doped ZnO films on nanofaceted Si templates

6.2.1.1 Introduction

Aluminium-doped ZnO – a transparent conducting oxide (TCO) is becoming increasingly popular, not only for the study of optical properties but as a window layer and top electrode, for next generation highly efficient silicon-based heterojunction solar cells[41-44]. An essential criterion to enhance the efficiency of silicon-based solar cells is to reduce the front surface reflection. However, commercial silicon wafers show surface reflection more than 30% [45]. Such a high level of reflection can be minimized by growing a suitable antireflection (AR) coating, preferably in the form of a TCO. On the basis of thin film interference property, these dielectric coatings reduce the intensity of the reflected wave. However, this approach needs a large number of layers to achieve well-defined AR properties. In addition, coating materials with good AR properties and low absorption in the ultraviolet (UV) range is rare in the literature. An alternative to the lone usage of dielectric coating is therefore, required that can overcome some of these difficulties.

An optimal antireflective surface should contain subwavelength features where the index matching at the substrate interface leads to improved AR performance. For instance, by using a surface texture on TCO (e.g. AZO) [46] and/or Si substrate[47] one can govern the light propagation and in turn the AR property due to the formation of graded refractive index [48,49]. In particular, for solar cell applications, a patterned AZO film on a flat silicon substrate shows a significant decrease in average reflectance up to 5% [50] whereas a thick AZO layer on silicon nanopillars is found to give an overall reflectance of ~10%[47]. In the latter case, a
higher photocurrent density was achieved (5.5 mA cm$^{-2}$) as compared to AZO deposited on planar silicon (1.1 mA cm$^{-2}$). It is, therefore, exigent to have more control on pattern formation and optimization of AZO thickness to achieve improved AR performance.

Majority of the patterning processes are based on conventional lithographic techniques [51]. As a result, these are time consuming and involve multiple processing steps. On the other hand, low energy ion-beam sputtering has shown its potential as a single step and fast processing route to produce large area (size tunable), self-organized nanoscale patterned surfaces [22]—compatible to the present semiconductor industry and thus, may be considered to be challenging to develop AR surfaces for photovoltaics.

In our study, we show the efficacy of one step ion-beam fabricated nanofacetted silicon templates [52] for growth of conformal AZO overlayer and correlate its thickness-dependent (in the range of 30-90 nm) AR property. We show that growth of an optimum AZO overlayer thickness can help achieving maximum reduction in surface reflectance. As a possible application of such heterostructures in photovoltaics, photoresponsivity of AZO deposited on pristine and faceted Si has also been investigated. The results show that by using nanofaceted silicon templates it is possible to enhance the fill factor ($FF$) of the device by a factor of 2.5.

### 6.2.1.2 Experimental

The substrates used in the experiments were cut into small pieces (area: 1 × 1 cm$^2$) from a p-Si(100) wafer. An ultrahigh vacuum (UHV)-compatible experimental chamber [_prevac, Poland] was used which is equipped with a 5-axes sample manipulator and an electron cyclotron resonance (ECR)-based broad beam, filamentless ion source [GEN-II, Tectra GmbH, Germany]. Silicon pieces were fixed on a sample holder where a sacrificial silicon wafer ensured a low impurity environment. The beam diameter and the fixed ion-flux were measured to be 3 cm and 1.3×10$^{14}$ ions cm$^{-2}$ s$^{-1}$, respectively. Corresponding to this flux of 500 eV Ar$^+$
ions, the rise in sample temperature is expected to be nominal from room temperature (RT). Experiments were carried out at an ion incidence angle of 72.5° (with respect to the surface normal) and for an optimized fluence of 3×10^{18} ions cm^{-2} to fabricate nanofaceted silicon templates. The substrates were immediately transferred to the sputtering chamber (base pressure 3×10^{-7} mbar) for growth of AZO overlayers. A commercial (purity 99.99%) target [Testbourne, UK] composed of ZnO:Al_{2}O_{3} (2 wt.%) was used for deposition of AZO films at RT and at an optimized angle of 50°. During film growth, the argon gas flow rate was maintained at 30 sccm resulting in the working pressure of 5×10^{-3} mbar. The distance from the sample to the target was 10 cm and the pulsed dc power was maintained at 100 W. Figure 6.8 shows a schematic representation of the process flow towards the synthesis of nanofaceted silicon and the growth of AZO overlayer on the same thicknesses (in the range of 30-90 nm) were measured by using a surface profilometer [Ambios, XP-200, USA].

Figure 6.8: Flow chart for ion-beam fabrication of nanofaceted Si followed by conformal growth of AZO films on the same.

Field emission scanning electron microscopy (SEM) [Carl-Zeiss, Germany] was employed to study the sample microstructures and to ensure the uniformity of the structures. Sample morphologies were studied by using an atomic force microscope (AFM) [Asylum Research, MFP3D, USA] in the tapping mode. AFM images were analysed by using WSxM and
Gwyddion softwares [27,28]. Crystallinity and phase identification of the films were investigated by x-ray diffraction (XRD) [Bruker, D8-Discover, Germany] whereas the optical reflectance measurements were carried out by using a UV-Vis-NIR spectrophotometer [Shimadzu, 3101PC, Japan] in the wavelength range of 300-800 nm with unpolarized light. A specular geometry was used for these measurements where the incident light fell on the target at an angle of 45° with respect to the surface normal. Photoresponsivity studies were performed out using a spectral response system [Sciencetech, Canada] under air mass 0 and 1 sun illumination conditions in the spectral range of 300-800 nm. The incident light power was measured with a calibrated silicon photodiode at wavelengths below 1100 nm and the spectra were normalized to the power. In the reflectance measurement, we recorded the data corresponding to specular reflectance values only. It may be mentioned that all the reflectance spectra shown in the present thesis do not contain any contribution from diffuse reflectance.

6.2.1.3 Results and discussion

Figure 6.9(a) shows the SEM image of a typical ion-beam fabricated silicon template under consideration, manifesting distinct faceted morphology with striations on its walls. Corresponding AFM image, shown in Fig. 6.9(b), indicates that the Si facets are oriented in the direction of incident ion-beam. Analysis of this image provides rms roughness value of 52.5 nm whereas the average silicon facet height turns out to be ~180 nm. Two-dimensional (2D) fast Fourier transform (FFT) image, obtained by using Gwyddion software, is depicted in the inset of Fig. 6.9(b) where a clear anisotropy in the surface morphology is visible along the direction perpendicular to the ion-beam projection onto the surface. One-dimensional (1D) power spectral density as well as autocorrelation function (not shown here), along both x- and y-directions, do not reveal any periodicity in case of Si nanofacets. This corroborates well with the absence of any distinct spots symmetrically spaced about the central spot seen in the FFT image. Figures 6.9(c) and (d) depict the morphologies of nanofaceted Si templates after
deposition of AZO overlayers having nominal thicknesses of 30 and 75 nm, respectively. Both

![Plan-view SEM images](image_url)

These images clearly manifest the conformal growth of AZO on Si facets albeit, with increasing AZO thickness, sharpness of the facets reduces and they gradually transform from conical shapes into rod-like structures. Figure 6.9(d) documents the existence of nanoscale grains on the conformally grown AZO facets.

The elemental composition of these samples was studied by energy dispersive x-ray spectrometry (EDS) analysis which does not reveal the presence of any metallic impurity in these facets. A representative EDS spectrum corresponding to the 60 nm-thick AZO film on
nanofaceted-Si is depicted in Fig. 6.10(a). Thickness dependent EDS study demonstrates that concentration of Zn increases with increasing film thickness, while that of silicon decreases rapidly [Fig. 6.10(b)].

Subsequent elemental mapping exhibits Zn-rich apex of the conformally grown AZO faceted structures. Morphological evolution for AZO overlayer more than 75 nm thick is not presented here since the reflectance minimum goes beyond the spectral range (will be discussed later).

Crystalline nature of the AZO overlayers was revealed from XRD studies [Figure 6.10(c)]; where the appearance of only one peak, in addition to the substrate silicon signal (not shown),
can be attributed to the oriented nature of grains. This peak, at all thicknesses, matches well with the (002) reflection of the hexagonal wurzite phase of AZO indicating a preferential growth along the c-axis [53]. The average grain size determined from Scherrer’s formula is seen to grow bigger with increasing AZO thickness [54]. This corroborates well with the grain size analysis performed on the basis of the SEM studies.

The key result is the change in surface reflectance with increasing AZO thickness on nanofaceted Si templates (Fig. 6.11). In particular, it presents the reflectance data of pristine and faceted silicon along with those obtained from AZO films of varying thicknesses [Fig. 6.11(a)]. Due to the faceted structures, the calculated average residual reflectance [55], over the spectral range of 300-800 nm, reduces by 58.5% (compared to that of pristine Si). It is evident from Fig. 6.11(a) that upon coating the Si template (nanofaceted Si substrate) by a 30 nm thick AZO film, it exhibits a low average residual reflectance of 6.4% whereas conformally grown 60 nm thick AZO film leads to a further reduction down to 3.1%. However, an increased film thickness of 75 nm causes a nominal increase in the average residual reflectance up to 3.8% which increases further for thicknesses higher than this. A careful observation of the reflectance spectra reveals that the local reflectance minimum of each spectrum (corresponding to different AZO film thickness) gets red shifted [Fig. 6.11(b)]. For instance, 30 nm thick AZO film shows reflectance below 1% for a spectral range of 385-445 nm with a local minimum of ~0.5% at 415 nm. Likewise, for the 60 nm thick overlayer, this range shifts to 530-655 nm and the minimum reflectance is found to be ~0.3% at 585 nm. Further increase in AZO layer thickness (75 nm) leads to the minimum reflectance of ~0.5% at 745 nm. Such shifts in the local minima were previously reported by Boden et al. [56] for an antireflective Si surface. Thus, one can infer that tunable AR property of conformally grown AZO films on nanofaceted Si templates can be achieved by varying the thickness and there exists a critical thickness (60
nm in the present case) which exhibits the best AR performance over the given spectral range (300 to 800 nm).

Figure 6.11: (a) Reflectance spectra corresponding to pristine-Si, nanofaceted-Si, and AZO overlayers grown on faceted Si having thicknesses of 30 nm, 60 nm, and 75 nm. (b) Reflectance spectra obtained from 30, 60, and 75 nm thick AZO films deposited on faceted Si where the dashed line corresponds to the domain of reflectance minima for different AZO layer thickness (all the reflectance spectra shown here do not contain any contribution from diffuse reflectance).

It may be mentioned that effect of the experimental geometry was tested by subsequent measurement of the surface reflectance after giving a perpendicular rotation to the samples. However, no difference in the reflectance values (within the experimental error) was observed in both cases. To understand this behaviour we calculated the average aspect ratio of the faceted structures (i.e. height : lateral dimension) along x- and y-directions which turned out to be 0.25
and 0.24, respectively. It is well-known that reflectance depends on the aspect ratio of the surface features [57].

Figure 6.12: Photoresponsivity spectra of 30 nm thick AZO overlayer grown on planar and nanofaceted Si in the spectral range of 300-800 nm. The inset shows the optical reflectance spectra for these two samples mentioned above.

Thus, the observed absence of change in surface reflectance, due to different directions of incident light, can be attributed to the comparable aspect ratio of the faceted structures along x- and y-directions.

Figure 6.12 shows RT photoresponsivity of two sets of samples, viz. 30 nm AZO deposited on pristine and faceted silicon. It is observed that the photoresponsivity reduces in case of the latter one in the projected wavelength range. Different parameters such as short circuit current densities ($J_{SC}$), open-circuit voltages ($V_{OC}$), and $FF$ for the above samples are summarized in Table 6.3 under air mass zero and 1 sun illumination condition for other AZO thicknesses as well. The $FF$ is defined as $FF = (V_M J_M) / (V_{OC} J_{SC})$ where $V_M J_M$ is the maximum power density.

From Table 6.3, one can see that the $FF$ increases by a factor of two in case of AZO overlayer grown on faceted silicon as compared to the one on pristine silicon, whereas $V_{OC}$ is found to be
half the value obtained from the latter one. In addition, $J_{sc}$ becomes one order of magnitude higher in case of AZO-coated faceted silicon and the same trend is followed for higher AZO thicknesses. From Table 6.3, it is observed that the $FF$ reaches maximum at 60 nm AZO on faceted silicon (0.361) as compared to others. This improvement in $FF$ can be attributed to the effective light trapping in the visible region in case of conformally grown AZO films on nanofaceted silicon template [58].

**Table 6.3**

<table>
<thead>
<tr>
<th>Sample</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (V)</th>
<th>$FF$</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 nm AZO on Pristine-Si*</td>
<td>1.24×10$^{-3}$</td>
<td>0.133</td>
<td>0.142</td>
</tr>
<tr>
<td>30 nm AZO on Nanofaceted-Si</td>
<td>3.0×10$^{-2}$</td>
<td>0.075</td>
<td>0.279</td>
</tr>
<tr>
<td>60 nm AZO-on nanofaceted-Si</td>
<td>5.35×10$^{-2}$</td>
<td>0.087</td>
<td>0.361</td>
</tr>
<tr>
<td>75 nm AZO on nanofaceted-Si</td>
<td>37.57×10$^{-2}$</td>
<td>0.055</td>
<td>0.252</td>
</tr>
</tbody>
</table>

* Higher AZO thicknesses (beyond 30 nm) deposited on planar silicon substrate did not show any significant photoresponsivity.

This would ensure the usage of more photo generated power leading to an increase in the cell efficiency. Such enhancement in light trapping is found to be directly associated with the enhanced AR property of the same film (inset of Figure 6.12). However, the reduced $V_{oc}$ can be attributed to the existence of defect centres in the native oxide at the AZO/Si interface and ion-beam produced traps on silicon facets. It may be mentioned that AZO/Si heterostructures, in general, yield low $FF$ values and can be improved by using nanofaceted silicon substrates [59]. Thus, our experimental results suggest that besides tunable AR property (Fig. 6.11), $FF$ can also be improved by adjusting the AZO overlayer thickness.

Compared to the inverted pyramid approach [60,61], which yields the reflectance values between 3 to 5% for an optimized AR coating thickness between 400 to 1000 nm, our results
show a better (by a factor of 10) performance with a smaller (30 to 75 nm) AZO film thickness. Among the available techniques reported in the literature, our novel approach of fabricating faceted nanostructures is simple and can be seamlessly integrated with the modern thin film solar cell technology for better photon harvesting with the help of proper understanding of AR property of AZO films. For a flat surface having an AR overlayer, using Fresnel’s reflection formula, we measured the reflectance at different wavelengths. It is observed that with varying film thickness the position of the reflection minima shifts, while a change in the refractive index modifies the amount of surface reflectance [62]. Although similar trends are quite evident, the experimentally observed average surface reflectance turns out to be much lower over the spectral range under consideration.

In order to explain these results, let us first try to understand the role of the Si template which is practically an ensemble of ion-beam fabricated self-organized conical nanofacets at the top of the Si substrate. It is known that a grating on any surface can be used to achieve arbitrary refractive index if the geometry of the grating structures can be tuned. For instance, if we consider a binary grating, its effective refractive index, $n_{\text{eff}}$, can be expressed as $n_{\text{eff}} = (n_1 - 1)DC + 1$, where $n_1$ is the refractive index of the grating and $DC$ is the duty cycle and is defined as the ratio of the grating line width to the grating period [63]. If the surrounding medium is taken as air and the grating is of the same material as the substrate, the optimized duty cycle (to meet the AR criterion) can be expressed as $DC = \sqrt{\frac{n_2 - 1}{n_2 - 1}}$, where $n_2$ is the refractive index of the substrate [63]. Such binary gratings are expected to exhibit the AR property over a very narrow spectral range. This range can be broadened by continuous tuning of the refractive index ($n_{\text{eff}}$) between the two surrounding media. This would essentially mean a continuous change in $DC$ along the depth (from the apex towards the base of the facets) of the grating lines, which is possible to be achieved by having tapered/conical gratings. When the grating and the substrate materials are the same, the matching of refractive index at the substrate interfaces can
exhibit highly improved AR property [64]. This explains the enhanced AR performance observed here for the faceted Si surface formed on the Si substrate. Following the same argument, further improved AR performance is expected due to the conformal growth of an AZO overlayer on nanofaceted Si template. Indeed, the experimental findings confirm the same where increasing AZO thickness leads to a systematic red shift in the reflection minima. However, such small variations in the thickness may not be sufficient to cause any significant difference in depth dependent change of the effective refractive index for the AZO coated faceted Si template which corroborates well with the experimentally measured reflectance minima values.

6.2.1.4 Conclusions

In conclusion, we show that conformally grown AZO films on ion-beam fabricated self-organized nanofaceted Si templates can work in tandem to yield improved AR performance. It is observed that tunable AR property can be achieved by varying the thickness of AZO overlayer and there exists a critical thickness (60 nm in the present case) which exhibits the best AR performance over the given spectral range (300 to 800 nm). Reduction in surface reflectance for Si templates can be understood in light of gradient refractive index effect arising from a continuous change in the effective refractive index along the depth (from the apex towards the base of the facets) and refractive index matching at the substrate interface because of self-organized nanofaceted Si structures. Following the same argument, further enhancement in the AR performance is observed due to conformal growth of AZO overlayers on Si templates. This is accompanied by a thickness-dependent systematic red shift in the reflection minima. The fabricated AZO/Si heterostructures, both on planar and faceted silicon, show significant photoresponsivity where thickness-dependent fill factor increases by a factor up to three owing to improved light absorption in the latter case. This study indicates that
conformally grown AZO overlayer on nanofaceted silicon may be a promising candidate as AR coatings by optimizing the process parameters.

6.2.2 Thickness-controlled photoresponsivity of ZnO:Al/Si heterostructures: Role of junction barrier height

6.2.2.1 Introduction

Metal-oxide-semiconductors (MOS) have attracted much attention in optoelectronic applications due to their unique optical and electrical properties [65]. For instance, ZnO is considered to be a promising material for light-emitting diodes, laser diodes, photodetectors, and solar cells [65]. Due to several issues like deep acceptor levels and low dopant solubility, reproducible fabrication of $p$-type ZnO for $p$-$n$ homojunctions is difficult and thus, it gives rise to the need for ZnO/Si heterojunctions. It may be noticed that the conductivity of $n$-type ZnO can be enhanced up to three to four orders of magnitude after doping with Group-III elements (especially Al) [43]. In fact, due to a mismatch in the work functions of Si (~4.2 eV) and AZO (~4.8 eV), a potential barrier is formed where the barrier height depends not only on the work functions but also on AZO thickness [66,53]. Although $I$-$V$ characteristics of AZO/Si heterojunctions are well-studied [66,53], effect of AZO thickness on the potential barrier at AZO/nanostructured-Si interface and in turn change in photoresponsivity is yet to be studied in a systematic manner. Since AZO films deposited on Si nanostructured surfaces show promising optical properties [47], it will be important to grow AZO overlayers on textured Si surface and study their optoelectronic properties.

Ion-beam induced self-organization process is a fast and cost-effective way to synthesize various nanopatterns over a large area in a single step [52]. In the present study, we have used ion-beam fabricated nanofaceted-Si as the template for growing AZO films of various
thicknesses (in the range of 30-75 nm). AZO/nanofaceted-Si heterojunction properties were investigated by employing current–voltage ($I$-$V$) and capacitance–voltage ($C$-$V$) measurements whereas the photoresponsivity of $n$-AZO/$p$-faceted-Si heterostructures were studied as a function of AZO overlayer thickness. In fact, as a novelty, we show AZO thickness-dependent tunable photoresponsivity of AZO/nanofaceted-Si heterojunctions and correlated this behaviour with decrease in corresponding junction barrier heights.

6.2.2.2 Experimental

In the present study, we used 500 eV Ar-ions to fall on $p$-Si surface at an oblique incidence of 72.5°, resulting in nanoscale facet formation of nanofaceted arrays at the surface [52]. A commercial target composed of ZnO:Al$_2$O$_3$ (2 wt.%) was used for pulsed dc magnetron sputter deposition of AZO films on nanofaceted-Si at room temperature with argon gas flow rate of 30 sccm (working pressure of 5×10$^{-3}$ mbar). The distance from the sample to the target was 10 cm, and the power was maintained at 100 W. Three different film thicknesses (in the range of 30 to 75 nm) were simultaneously deposited on nanofaceted as well as pristine Si substrates [53]. Field emission gun scanning electron microscopy (FEGSEM) [Carl Zeiss, Germany] and atomic force microscopy (AFM) [Asylum Research, USA] were employed to study the respective sample microstructure and surface morphology. For each sample, several AFM images were collected from various places (including the edges and the central part of the films), confirming the homogeneity of our films. AFM images were analyzed by using Gwyddion software [28]. Photoresponsivity studies were carried out by using a spectral response system [Scicentech, Canada] under air mass 0 and 1 sun illumination conditions in the spectral range of 300 to 800 nm. Silver paste (~2 mm in diameter) was used to make electrical contacts on the top of AZO films and the back side of the Si substrates. Formation of Ag/AZO/nanofaceted-Si/Ag heterostructure diodes was verified by taking $I$-$V$ characteristics using a source meter [Keithley 2410]. In addition, the junction barrier height was investigated
by performing capacitance-voltage (C-V) measurements using a precision LCR meter [HP 4284A].

6.2.2.3 Results and discussion

Figures 6.13(a) and (b) show AFM images corresponding to nanofaceted Si substrate and 75 nm AZO film grown on the same. It is observed that with increasing film thickness, the sharp Si nanofacets transform into a bit rounded ones. However, no significant change in the root mean square (rms) surface roughness is observed with increasing film thickness (Table 6.4).

Table 6.4 List of parameters calculated from AFM, I-V, and C-V measurements

<table>
<thead>
<tr>
<th>Sample</th>
<th>AFM</th>
<th>I-V</th>
<th>C-V</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>AZO on faceted Si*</td>
<td>Roughness (nm)</td>
<td>Turn-on potential (V)</td>
<td>Series resistance (kΩ)</td>
<td>Indeality factor (η)</td>
</tr>
<tr>
<td>30 nm</td>
<td>49.53</td>
<td>2.01</td>
<td>48.8</td>
<td>2.3</td>
</tr>
<tr>
<td>60 nm</td>
<td>52.48</td>
<td>1.42</td>
<td>10.4</td>
<td>2.8</td>
</tr>
<tr>
<td>75 nm</td>
<td>51.7</td>
<td>0.93</td>
<td>1.1</td>
<td>3.48</td>
</tr>
</tbody>
</table>

*Nanofaceted Si has rms roughness of 52.21 nm
Figure 6.13: AFM images corresponding to (a) nanofaceted-Si template and (b) 75 nm AZO grown on nanofaceted-Si. Line profiles drawn on (a) and (b) are shown in (c) and (d) shows a high-resolution SEM image of (b). Line profiles drawn on Figs. 6.13(a) and (b) confirm the conformal growth of AZO films [Fig 6.13(c)]. In addition, a high-resolution plan-view SEM image, corresponding to Fig. 6.13(b), is also shown in Fig. 6.12(d) where a magnified portion of the facet-apex ensures the conformity and the closely packed granular nature of the AZO film (with average grain size ~25 nm).

Prior to the electrical characterization of AZO/nanofaceted-Si heterojunction, the Ohmic nature of the silver contact with AZO was confirmed from the linear I-V characteristics [53]. However, I-V characteristics of all the Ag/AZO/nanofaceted-Si/Ag heterojunction diodes show a rectifying property [Fig. 6.14(a)] where schematic view of such a diode is depicted in the inset. It is seen that with increasing AZO thickness, the turn-on potential decreases systematically from 2.02 to 0.93 V. The diode ideality factor (η) and its series resistance (R_s) were calculated and listed in Table 6.4 where one sees a clear increase in η with increasing AZO overlayer thickness, indicating a degradation of diode characteristics. Due to a large lattice mismatch between the AZO layer and Si(100) substrate, dislocations appearing at the AZO/Si interface can lead to an increase in η. Since the AZO/Si interface plays an important role in carrier injection, we believe that AZO thickness-dependent increase in η is most likely associated with the minority carrier injection and recombination [53]. This is consistent with the increase in reverse saturation current (I_0) with increasing AZO film thickness which in turn takes part in suppressing the turn-on potential by decreasing the barrier height at the AZO/Si interface. The barrier height, \( \varphi_B \), at a temperature \( T \) can be determined from \( I_0 = A^*S^*T^2 \exp \left( -\varphi_B/k_B T \right) \), where \( S \) is the surface area of the diode, \( k_B \) is Boltzmann constant, and \( A^* \) is Richardson constant [53]. Since the presence of a thin native SiO_x at the interface of AZO/nanofaceted-Si heterojunction cannot be avoided, the calculated \( \varphi_B \) may be incorrect. Thus, in order to determine the actual \( \varphi_B \), C-V measurements, at a frequency of 1 MHz, by sweeping 6 to −6 V...
were carried out. Figure 6.14(b) shows the $1/C^2-V$ plot where the extrapolated straight line intercept of $1/C^2$ on the $V$-axis turns out to be the measure of $\varphi_B$. The calculated values of $\varphi_B$ corresponding to different AZO overlayer thicknesses are listed in Table 6.4 where an increasing barrier height results due to a decrease in the film thickness. Thus, the reduction in the turn-on potential as a function of AZO thickness (mentioned above) in case of AZO/Si heterojunction diodes can be attributed to the reduced barrier height. It is noticed that a similar behavior, viz. reduction in the turn-on potential was reported for AZO films deposited on pristine Si substrate as well [53]. However, the turn-on potential obtained in the present case is reduced by a factor of 1.5 in comparison to the same thickness of AZO films deposited on pristine Si substrate which may be attributed due to interface effect arising from different morphologies of the substrates.

![Figure 6.14](image)

**Figure 6.14:** (a) Thickness-dependent nonlinear $I-V$ characteristics where the inset shows a schematic view of an AZO/Si heterojunction diode. (b) $1/C^2-V$ characteristics for different AZO film thicknesses.

In order to understand the role of the barrier height, in particular for optoelectronics applications, we measured the photoresponsivity at different wavelength ranges. It is known that AZO/Si heterostructure devices, in general, yield low photoresponsivity. Figure 6.15
shows the photoresponsivity spectra under a forward bias of 0.5 V corresponding to different AZO overlayer thicknesses where an increment in the photoresponsivity with AZO thickness is observed. As a matter of fact, the energy band-diagram of AZO/Si heterojunction, under forward bias, shows a valence band offset of 2.55 eV which is greater than the conduction band offset of 0.4 eV [66]. Since the transmittance of AZO on a glass substrate was measured to be ~80% in the visible range, visible light gets absorbed in the underlying p-Si substrate (decorated by nanofaceted arrays on its surface) after transmitting through the AZO overlayer and generates electron-hole pairs inside Si. The electric field drives the photo-generated holes towards n-AZO but they face the potential barrier across the interface of the heterojunction. It is evident from the inset of Fig. 6.15 that the barrier height decreases with increasing AZO overlayer thickness, and hence, the photo-generated holes can overcome the interface barrier more easily at a higher AZO thickness (e.g. 75 nm) in comparison to the lower one (30 nm).

Figure 6.15: Thickness-dependent photoresponsivity spectra in the wavelength range of 300-800 nm. The inset shows variation in the barrier height and turn-on potential as a function of AZO thickness.
The easy conduction of photo-generated carriers leads to the overall enhancement in the photoresponsivity as a function of AZO overlayer thickness.

### 6.2.2.4 Conclusions

In summary, we fabricated AZO/Si heterojunction diodes where ion-beam sputtered nanofaceted $p$-Si templates were used for conformal growth of $n$-AZO overlayers by pulsed dc magnetron sputtering. $I$-$V$ characteristics and photoresponsivity were studied as a function of film thickness. It is observed that with increasing AZO thickness, turn-on potential of the present $n$-AZO/$p$-Si diodes decreases (by a factor of ~2) whereas photoresponsivity enhances significantly (up to a factor of ~5). The observed thickness-dependent photoresponsivity is attributed to the decrease in AZO/nanofaceted-Si junction barrier height. The results are quite promising for the fabrication of AZO-based advanced optoelectronics devices.

### Bibliography

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