CHAPTER 5

5. Tunable optoelectronic properties of nanopatterned-Si surfaces

In this chapter, we have demonstrated the usage of nanopatterned-Si surfaces towards tuning antireflection (AR) and photoluminescence (PL) properties. In particular, nanofaceted-Si surfaces were used to study corresponding AR and PL properties. Furthermore, as a case study, Si nanofacets were employed to study field emission properties.

5.1 Tailoring room temperature photoluminescence of antireflective Si nanofacets

5.1.1 Introduction

Silicon nanostructures have drawn a lot of attention in recent years because of its unusual quantum confinement (QC) properties which yields unique structural, optical, and electronic behaviours [1], viz. single electron devices [2], sensors [3], and cold cathodes for field-emission displays [4]. In bulk silicon, direct inter-band transitions are not allowed by the momentum conservation law and to make this happen, phonon absorption is required [5]. An alternative way to overcome this difficulty is to modify the electron dispersion equations for valence and conduction bands by controlling the size of Si nanostructures [6]. Besides QC-mediated photoluminescence (PL), Si-O defect states (generally exist at the surface of Si nanoclusters or at the Si/SiO$_x$ interface) also take part in radiative emission, as reported earlier [7-9]. Although the origin of PL emission from silicon nanostructures is a much debatable topic, silicon based UV-emitting materials always draw special attention since optical data
storage devices often need light sources with shorter wavelengths, preferably in the UV range, for improving the storage density.

Over the last two decades, different types of Si-based nanocrystalline materials were prepared which exhibit PL comparable to porous silicon [10]. Although most of these studies are based on luminescence in the visible range, few studies exist where blue and UV light emission from Si nanostructures are addressed [11,12]. Despite much progress in the fabrication and luminescence property of Si nanostructures, one of the key challenges is to improve the emission efficiency which is largely dependent on the absorbed photons. Different approaches are followed to improve light extraction ratio (which in turn enhances the luminescence efficiency) by using photonic crystal structures, surface plasmon polariton etc. [13-15]. However, these processes are complex and involve multiple fabrication steps. On the other hand, an alternative way to enhance absorption of light and in turn achieve higher emission efficiency is to use textured/rough surfaces which are effective to reduce reflection loss, leading to an improved light extraction ratio [16,17]. In fact, for a planar surface, a large difference in the refractive index between Si and air causes enhanced Fresnel reflection of the incident light from air to the substrate. This makes a diminishing intensity of the incident light available for absorption, leading to a large optical loss. In contrast, this loss gets minimized for textured surfaces – inspired by biomimetic moth-eye structures – where the surface micro/nano-structures lead to a gradual change in the effective refractive index between air and the substrate [18]. Recently, successful attempts have been made to fabricate light emitting diodes based on nanostructured surfaces where light extraction efficiency is seen to be enhanced [19-21].

In this work, we emphasize on the importance of antireflection (AR) property of nanofaceted-Si surfaces, fabricated by low energy argon ions, to achieve tunable photoluminescence at room temperature (RT). Si surfaces having nanofacets of different
heights were prepared at various ion fluences and two different angles of incidence, viz. 70° and 72.5°. In both cases, the observed PL intensity from these nanostructures increases with ion fluence whereas an opposite trend is noticed for surface reflectance. Origin of such PL emission from the faceted-Si substrates is attributed to argon-ion activated $E^-$ centres and Si-O related states present at the interface of Si/SiO$_x$. In particular, the observed PL peak at 368 nm has been correlated to the -SiO$_3$ group where the presence of different oxides at the surface has been confirmed by x-ray photoelectron spectroscopic (XPS) studies. Enhancement in the PL intensity has further been ascribed to the improved light absorption (i.e. reduction in surface reflectance) due to the presence of silicon nanofacets at the surface.

5.1.2 Experimental

Silicon samples, used in the present experiments, were sliced out (1×1 cm$^2$) from a $p$-type Si(100) wafer. A UHV-compatible experimental chamber, equipped with an electron cyclotron resonance based broad beam ion source, was used to prepare nanofaceted structures on Si surfaces. The chamber base pressure was below 5×10$^{-9}$ mbar and the working pressure was maintained at 3×10$^{-4}$ mbar. Substrates were fixed on the sample platen of a 5-axes manipulator which was first covered by a sacrificial Si wafer (taken from the same lot of the substrate) to ensure a low impurity environment. Samples were exposed to 500 eV Ar-ions at two incidence angles, viz. $\theta$=70° and 72.5° (with respect to the surface normal) at RT. The beam diameter was measured to be 3 cm which corresponds to a fixed ion flux of 1.3×10$^{14}$ ions cm$^{-2}$ s$^{-1}$ (corresponding to a target current of 160 μA) in a plane normal to the ion-beam direction. Experiments were carried out for fluences ranging from 5×10$^{17}$ to 2×10$^{18}$ions cm$^{-2}$.

Following Ar-ion exposure, the samples were imaged by ex-situ atomic force microscopy. All the AFM images were analyzed by using the WSxM software [22]. In addition, microstructural study was performed by using high-resolution transmission electron microscopy.
microscopy (HRTEM). The surface chemical property was studied by x-ray photoelectron spectroscopy (XPS) using Mg-Kα radiation source (hν = 1254 eV). Optical reflectance studies were carried out by using a UV-Vis-NIR spectrophotometer at 45° incidence in the wavelength range of 300-800 nm. Room temperature PL measurements were performed at RT by steady state fluorescence spectrometer equipped with a 325 nm He-Cd laser.

5.1.3 Results and discussion

Figure 5.1(a) and (b) represents three-dimensional (3D) AFM topographic images obtained from samples after exposure to Ar-ions at θ=70° and 72.5° at the highest ion fluence of 2×10^{18} ions cm^{-2}. It is observed that nanofaceted structures (conical) evolve up to 2×10^{18} ions cm^{-2}. Similar morphological evolution takes place for lower fluences as well (images not shown). Formation of such faceted morphology is observed only over this limited angular window [23]. Figure 5.1(c) depicts the evolution of average facet heights as a function of ion fluence at θ=70° and 72.5° where an increasing trend is observed for both cases. Such nanofaceted structures evolve due to a transition from ripple (which are formed at fluences below 5×10^{17} ions cm^{-2}).

As a matter of fact, with an increase in the ratio of ripple height (h_0) to ripple wavelength (λ), the local angle of incidence along the ripple pattern eventually become so large that the upstream part of the ripple gets shadowed from the incoming ion-flux by the preceding peak. Thus, the limiting condition to avoid such shadowing of incident beam is [24]:

\[ \tan \left( \frac{\pi}{2} - \theta \right) \geq 2\pi \left( \frac{h_0}{\lambda} \right) \]

where θ is the angle of incidence. According to this condition, if the ratio (h_0/λ) exceeds a threshold value, troughs of a sinusoid will not be eroded further but instead erosion will take place at the crest. This in turn can give rise to a faceted structure [23].
Figure 5.1: Three-dimensional AFM micrographs corresponding to samples exposed to ion fluence of $2 \times 10^{18} \text{ cm}^{-2}$ at incidence angle of 70° (a) and 72.5° (b). Figure 1(c) depicts the evolution of average facet heights as a function of ion fluence at $\theta = 70^\circ$ and 72.5°.

In the present case, beyond the fluence of $2 \times 10^{17} \text{ ions cm}^{-2}$, the condition of shadowing sets in and thus, it is expected to get faceted nanostructures as mentioned above. In addition, with increasing fluence, faceted nanostructures demonstrate coarsening behaviour. The observed facet coarsening is attributed to a mechanism based on reflection of primary ions from facets [23,25]. Recently, Engler et al. also reported formation of similar kind of faceted nanostructures on Si surface by using 2 keV Kr-ions at comparable fluences [26] and quantified the obtained faceted nanostructures in terms of facet height and slope distribution. It was demonstrated that with increasing ion fluence, the facet angle did not show any meaningful change. It may be mentioned that, we also observed the similar trend for facet angle as a
function of ion-fluence (the upstream facet angle becomes constant at 9° for both $\theta = 70^\circ$ and $72.5^\circ$) by using the SPIP software [27].

![XTEM image showing silicon facets fabricated by using 500 eV Ar-ions to the fluence of $5\times10^{17}$ cm$^{-2}$. The black circles depict the zones where $a$-Si and native oxides are present. Inset shows the FFT of the same image which reveals presence of different crystallographic planes.](image)

Microstructural investigations were also carried out by cross sectional transmission electron microscopy (XTEM). Figure 5.2 depicts a high-resolution XTEM image of such a faceted surface which shows the clear presence of lattice fringes, indicating the formation of crystalline facets. A careful observation reveals the presence of amorphous patches (marked by yellow loops) around the apex of the facets, albeit they are absent along both the sidewalls. This was confirmed by looking at a large number of frames. These patches may result from either ion induced amorphization of Si or the presence of native oxides.

In order to understand the fluence-dependent change in surface chemical properties, XPS studies were carried out for selective samples. Figures 5.3(a)-(c) show the Si 2$p$ spectra of pristine- and nanofaceted-Si samples exposed to the fluences of $5\times10^{17}$ and $2\times10^{18}$ ions cm$^{-2}$ (for $\theta=72.5^\circ$).
Figure 5.3: 2p core level Si XPS spectra taken from (a) Pristine-Si and samples exposed to ion fluences of (b) 5×10^{17}, (c) 2×10^{18} cm^{-2}, respectively.

The Si 2p core level spectrum, corresponding to the pristine sample, shows the presence of silicon oxides (Si^{1+} in the form of SiO_{3}, and Si^{2+} in the form of Si_{2}O_{3}) along with some proportions of SiO_{2} and Si-OH. The Si 2p spectrum corresponding to the fluence of 5×10^{17} ions cm^{-2} was deconvoluted into five peaks located at 98.25±0.15, 99.77±0.15, 101.59±0.15, 102.97±0.15, and 104.76±0.15 eV which are assigned to Si, SiO_{3}, Si_{2}O_{3}, SiO_{2}, and Si-OH bonds, respectively [28]. On the other hand, O1s core level spectrum for the said fluence shows bonding with SiO_{x} and H_{2}O. For the highest fluence of 2×10^{18} ions cm^{-2}, a similar trend is observed although Si concentration is little higher compared to that at the lowest fluence case. Relative amount of the respective components in the pristine and irradiated samples, determined from XPS analyses, are listed in Table 5.1. The survey spectra (not shown) at all fluences did not reveal the presence of any Fe signal from nanofaceted samples. This is
expected for the chosen experimental geometry where a sacrificial Si wafer was used to cover the entire sample platen (as described in the experimental section and Ref. 25) to avoid having impurity-induced nanostructure formation at such a glancing incidence angle. Similar results are obtained for $\theta=70^\circ$ (spectra not shown) as well. Thus, the amorphous patches at the facet apexes mostly consist of native oxide layer (SiO$_x$) which matches well with the prediction made on the basis of XTEM image shown in Fig. 5.2.

**Table 5.1:** Chemical compositional analyses using XPS

<table>
<thead>
<tr>
<th>Sample</th>
<th>Binding energy (eV)</th>
<th>Chemical composition</th>
<th>Concentration (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine-Si</td>
<td>98.2</td>
<td>Si$^0$, Si elemental</td>
<td>46.58</td>
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<tr>
<td></td>
<td>99.78</td>
<td>Si$^{1+}$, SiO$_3$</td>
<td>15.92</td>
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<tr>
<td></td>
<td>101.51</td>
<td>Si$^{2+}$, Si$_2$O$_3$</td>
<td>19.98</td>
</tr>
<tr>
<td></td>
<td>102.94</td>
<td>Si$^{4+}$, SiO$_2$</td>
<td>14.61</td>
</tr>
<tr>
<td></td>
<td>104.76</td>
<td>Si-OH</td>
<td>2.91</td>
</tr>
<tr>
<td>Si irradiated with 5×10$^{17}$Ar$^+$ cm$^{-2}$ at $72.5^\circ$</td>
<td>98.22</td>
<td>Si$^0$, Si elemental</td>
<td>36.58</td>
</tr>
<tr>
<td></td>
<td>99.79</td>
<td>Si$^{1+}$, SiO$_3$</td>
<td>19.19</td>
</tr>
<tr>
<td></td>
<td>101.59</td>
<td>Si$^{2+}$, Si$_2$O$_3$</td>
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<td>Si$^{4+}$, SiO$_2$</td>
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</tr>
<tr>
<td></td>
<td>104.7</td>
<td>Si-OH</td>
<td>7.41</td>
</tr>
<tr>
<td>Si irradiated with 2×10$^{18}$Ar$^+$ cm$^{-2}$ at $72.5^\circ$</td>
<td>98.24</td>
<td>Si$^0$, Si elemental</td>
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<tr>
<td></td>
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<td>Si-OH</td>
<td>4.59</td>
</tr>
</tbody>
</table>

Figure 5.4(a) presents the change in surface reflectance with increasing ion fluence in the range of 5×10$^{17}$-2×10$^{18}$ ions cm$^{-2}$ for $\theta=72.5^\circ$. It is observed that the reflectance decreases with increasing fluence. For instance, the reflectance at 550 nm reaches the values of 40% (for 5×10$^{17}$ ions cm$^{-2}$), 38% (for 1×10$^{18}$ ions cm$^{-2}$), and 26% (for 2×10$^{18}$ ions cm$^{-2}$). A similar trend is observed (reflectance reduces up to 31% for the fluence 2×10$^{18}$ ions cm$^{-2}$) in case of $\theta=70^\circ$ incidence angle (spectra not shown). Thus, it can be inferred that argon-ion induced topographically modulated Si surfaces (having faceted nanostructures) can manifest variable degree of AR property which is dependent on angle of incidence of ions and fluence.
Figure 5.4: (a) Reflectance study corresponding to Pristine-Si and samples exposed to four different ion fluences, viz. $5 \times 10^{17}$, $1 \times 10^{18}$, $1.5 \times 10^{18}$, and $2 \times 10^{18}$ cm$^{-2}$ for incidence angle of $72.5^\circ$, (b) facet height versus percentage area covered by the faceted structures extracted by using SPIP software from the respective AFM images shown in Fig. 1, and (c) schematic of the refractive index profile from air to Si substrate due to the presence of a facet.

In order to correlate the change in AR property with the surface morphology observed at two different $\theta$-values and Ar-ion fluences, we used SPIP software [27] to calculate the percentage area covered by the Si faceted structures with respect to air and plot it against the corresponding facet height at different fluences [Fig. 5.4(b)]. This shows an increasing trend in the surface height with decreasing percentage area covered by the facets. Thus, in our case, a faceted surface has a gradually varying Si-fraction from top (100% air: 0% Si) to bottom (0% air: 100% Si). This is further supported by the plots shown in Fig. 5.1(c) where facet height increases as
a function of ion fluence. Since a gradual change in facet height leads to the gradual variation in percentage area covered by the facets from top (100% air: 0% Si) to bottom (0% air: 100% Si), the observed AR property of nanofaceted-Si substrates can be understood in terms of well-known graded refractive index effect [29]. Corresponding schematic diagram of the refractive index profile from air to Si substrate due to the presence of a facet is shown in Fig. 5.4(c) where the presence of small amount (as compared to total facet) of amorphous-Si and native oxides at the apex was neglected. This gradual variation in refractive index can effectively eliminate the reflected light across a wide spectrum [29]. In the present case, with increasing sputtering time, facet dimensions become larger [as observed from Fig. 5.1(c)] which improves the antireflection over a wide spectral range.

The PL spectra of Si-nanofacets are presented in Fig. 5.5. In case of $\theta=72.5^\circ$, PL intensity is the weakest for the lowest fluence whereas it becomes the strongest at the highest fluence. It is observed that several PL peaks are located in the energy range of 3.39-2.67 eV (365-465 nm). Figure 5.5 illustrates that for the fluence of $5 \times 10^{17}$ ions cm$^{-2}$, a small shoulder appears at 373.5 nm along with a clear peak at 371 nm. With increasing fluence up to $2 \times 10^{18}$ ions cm$^{-2}$, a blue shift (~2.5 nm) is observed which is accompanied by the appearance of a less intense peak is detected at 396 nm. The inset of Fig. 5.5 shows the PL spectrum of a pristine-Si sample where no other PL peak is observed except a small hump at around 370 nm. This indicates that the origin of 371 nm PL band, in our case (including pristine-Si), may be related to the native oxide layer formed on top of the crystalline-Si. For UV light emission from Si-based nanostructures, two possible mechanisms are proposed. One is based on quantum size effect, which says that the excitation occurs between the quantized levels of nanocrystallites and the recombination happens either directly between the same levels or at the nanocrystalline surface/interface states after a relaxation process [30-33]. The other possibility is the presence of Si-O related species which governs the whole excitation and recombination processes [34-38].
To understand the origin of light emission from silicon nanostructures, we first explore the possibility of nanostructure-driven quantum confinement effect in silicon. For example, the model described by Zheng et al. [12] calculates the electronic states and optical transition matrix elements of Si quantum tips in a large energy range which yields transitions in the energy range of 2-4 eV. In another work, Adachi et al. reported UV PL emission at RT from porous silicon where they have attributed the results to the reduction in the $E_1$ critical point from two-dimension (2D) to zero-dimension (0D) due to quantum size effect [39]. As compared to silicon quantum tips or nanocrystals in case of faceted silicon, the apexes have the dimension in the range of 3-10 nm (Fig. 5.2) and they grow in the (001) direction. Thus, apparently, quantum confinement may play a role for the observed PL emission in the present case. In that case, one would expect a broad PL band due to a large distribution of the quantum tips and sizes. However, neither broadening nor blue shift of the PL peak in the UV region is
observed in our case and hence, the possibility of quantum confinement in the present study may be ruled out. Thus, in our case Si-O related defects seem to be more important for generating light emission. The UV PL band at 365 nm (in our case 370±2 nm) was attributed to the hole-trapped $E'$ centres (O$_3$≡Si) by Kim et al. [40]. In this study, XPS measurements reveal the presence of $E'$ centres in the form of O$_3$≡Si for both pristine and ion-irradiated samples and the corresponding concentrations are given in Table 5.1. Although SiO$_3$ (concentration 18.76%) is present in pristine-Si, it does not give rise to any strong 368 nm PL. On the other hand, one can strengthen this emission by exposing to 500 eV Ar-ions. Thus, it can be inferred that the $E'$ centres become more active due to the presence of Si nanofacets formed under argon-ion exposure because of the increased surface-to-volume ratio of the nanofacets. The small peak that appears at ~373 nm shows the similar behaviour and should be related to the same mechanism stated above.

Let us now try to explain the origin of the 396 nm emission from nanofaceted-Si structures. UV emission from porous silicon was reported earlier by Kanjilal et al. [41] where they reported on the 396 nm PL band and explained it on the basis of QC-luminescence centre model [42]. In addition, the role of fluorine related defects was also addressed. In the present case, we do not observe any fluorine related peak from XPS analysis which indicates that the observed emission at 396 nm should be related to the luminescence centres present in the vicinity of the silicon nanostructures. As mentioned by Qin et al. [42], there is a possibility of lack of non-radiative recombination centres inside the nanoscale objects of Si and therefore, radiative recombination takes place through the luminescence centres present outside Si nanostructures. According to this, the light emission takes place in two steps: Firstly, photoexcitation takes place inside Si nanostructures and subsequently the excited electrons and holes tunnel into the surrounding SiO$_x$ layers [42]. Secondly, the electrons and holes recombine radiatively via luminescence centres (LCs) in the neighbourhood. The aforementioned
discussion is also true in the present case, showing the PL signal at 396 nm for an excitation wavelength of 325 nm. As discerned from the XTEM image and XPS studies, the apexes of the faceted nanostructures are rich in SiO$_x$. Thus, the neutral oxygen vacancy sites located in the peripheral SiO$_x$ (on the top of the Si facets) can work as the LCs and give rise to the near-UV emission. Another possible explanation would be the formation of interconnects with the crystalline-Si nanostructures due to the diffusion of oxygen atoms. Kanemitsu et al. [43] reported that in case of oxidized porous silicon, amorphous SiO$_2$ layer on crystalline-Si core may give rise to PL emission in the range of 310-413 nm. Actually, at the interface of SiO$_2$/Si, electronic states are created due to the presence of the amorphous layer. With increasing temperature, oxygen atoms can diffuse into the crystalline layer and subsequently form bridges or interconnected silicon atoms. According to Kanemitsu et al., the inter-connected Si structure has a direct band gap of 3-4 eV which can give rise to blue light emission. Due to a large mismatch in the band gaps between interface and the outer surface, carriers may get confined in the Si-core. The same group reported that the corresponding blue emission decayed with a time constant of 650 ps [43]. Following this argument, we propose here that ion-exposure provides sufficient energy to oxygen atoms at the surface to inter-diffuse in the silicon matrix and to form bridges which give rise to the 396 nm emission line (in case of all ion-irradiated samples). To validate our claim further, time-resolved PL measurements were performed at an excitation wavelength of 375 nm by using a pulsed diode laser corresponding to the peak observed at 396 nm. The time constant turns out to be 347 ps which is close to the value obtained in case of porous silicon [43]. Thus, in the present case, it is difficult to point out the dominant mechanism (for UV PL emission) between these two.

Apart from the above-mentioned PL bands, appearance of twin peaks in the blue (449 and 460 nm) region is observed explicitly in case of argon-ion irradiated Si samples. It may be mentioned that the PL band at 468 nm PL band is thoroughly studied in case of silica glass and
ion implanted silicon [44-46]. This blue emission generally corresponds to the photo-absorption of neutral oxygen vacancies (O3≡Si-Si≡O3) and diamagnetic radiative recombination centres [47]. Thus, oxygen vacancies can play a crucial role in generating blue light emission. Origin of oxygen vacancies in Si are governed by different factors. For instance, Friebele and Griscom showed that oxygen vacancies are generated from the energetic electrons in the ionization cascade during irradiation process [48]. In another study, Devine et al. discussed oxygen vacancy generation process during ion bombardment [49]. Absorption of photons of energy higher than the band gap of SiO2 generates electron-hole pairs, a substantial portion of which gets converted to excitons. These excitons become the so-called self-trapped excitons when they get localized within the material by defects in the material. The radiative recombination of self-trapped excitons can produce blue (2.7 eV) PL emission [49]. Following the above discussion, oxygen vacancies generated during Ar-ion irradiation process might be acting as trap centres for photo-generated excitons in SiO2 (as evident from XPS analysis). These trapped excitons subsequently recombine to give rise to PL bands at 449 and 460 nm.

The key result in the present case is the observation of drastic enhancement in overall PL intensity (at RT) as a function of ion-fluence. We explored the possibility of correlating this behaviour to the improved antireflection/enhanced absorption property of the nanofaceted-Si. This seems more plausible in our case as XPS analyses (Fig. 5.3) do not reveal much difference in the concentration of chemical species in the pristine and ion-irradiated Si samples. Thus, it is clear that the observed enhancement in the PL intensity is not due to the variation in the concentration of different defect states but something else. It has been reported that light extraction from Si-based materials can be enhanced by making use of textured surfaces which show enhanced luminescent property by surface roughening process [21]. As discussed above, the surface reflectance is significantly suppressed by using nanopatterned structures (Fig. 5.4), the light emission should effectively increase due to the antireflection effect over a wide
spectral range. Since the reflection of incident light in the UV region also reduces [as observed from Fig. 5.4(a)], the more incident light can be absorbed in the Si nanofacets to excite much more electron-hole pairs leading to a stronger emission. It may be noted that the excitation wavelength (325 nm) is in the UV region and from the reflectance measurements [Fig. 5.4(a)], we observe a significant improvement in the AR property as a function ion fluence, in the UV region as well. Thus, the excitation light (He-Cd laser, 325 nm) gets benefitted from this antireflection property and maximum increment in the emission intensity is observed in the spectral range of 360-380 nm. Thus, the improved AR property of nanofaceted-Si contributes to the significant enhancement in the PL intensity particularly in the UV region.

5.1.4 Conclusions

In conclusion, anion-fluence dependent tunable room temperature PL emission is demonstrated from nanofaceted-Si structures produced by 500 eV argon ion bombardment at oblique incidences. Origin of this UV PL emission is explained by taking into account argon-ion activated $E'$ centres and Si-O related states present at the interface of Si/SiO$_x$ nanofacets. On the other hand, emission in the blue region corresponds to the self-trapped excitons localized at the argon-ion induced oxygen vacancies at the surface of crystalline nanofacets. The enhancement in the overall PL intensity is attributed to the decrease in surface reflectance as a function of fluence due to the presence of textured surfaces (decorated with nanofacets). Thus, our experimental results show that the intensities of light emission of Si-based devices can be improved by using nanoscale textured surfaces. The present study indicates that silicon nanofacets might be a good candidate both as a functional silicon nanostructure and as a template for assembling silicon-based nanocomposites in fabricating optoelectronic nanodevices.
5.2 Field emission from nanofaceted-Si: Role of native oxide

5.2.1 Introduction

Contemporary technological research is based on the ability to manipulate the smallest unit of matter, i.e. atom in a precise way in order to obtain an exceptional performance. In doing so, engineering in nanoscale plays a critical role in today’s technology due to its structural dependency on physical properties. For instance, the electron transport mechanisms show different behaviour in case of three-dimensional (3D), two-dimensional (2D), and one-dimensional (1D) structures [50-52]. Taking this into consideration, it may be mentioned that electron tunnelling is highly influenced by the physical and geometrical properties of a nanomaterial [53-57]. In general, electrons from solids get emitted in vacuum under the thermal excitation (i.e. thermionic emission) or by applying an electric field [i.e. field emission (FE)]. However, most of the thermionic emission-based devices suffer from the problems of stability issues and heating effects [58]. Therefore, for room temperature operation, cold cathode emitters have emerged as promising candidates. Materials with high aspect ratios such as nanotubes, nanowires, and nanorods demonstrate excellent electron emission characteristics [59-61]. The enhanced electric field at the tips reduces the potential barrier at the metal-vacuum interface, which can be described as the zero electric field work function energy, $\phi$, so that electrons can tunnel from the solid into vacuum, enabling the Fowler-Nordheim (FN) tunnelling [62,63]. Generally, FE is defined by the Fowler-Nordheim (FN) equation defined as [62]:

$$ J = A \left( \frac{\beta^2 E^2}{\phi} \right) \exp \left( -\frac{B \phi^{3/2}}{\beta E} \right) $$

(1)

where $J$ is the emission current density (A m$^{-2}$), $E$ is the mean electric field between the electrodes (V $\mu$m$^{-1}$), and $\phi$ is the work function (eV). The constants are $A=1.56 \times 10^{-10}$ A V$^{-2}$ eV and $B=6.83 \times 10^{3}$ V eV$^{-1.5}$ $\mu$m$^{-1}$. The enhancement factor, $\beta$, depends on tip-sample geometry.
which is 1 for a flat surface and higher for other geometries. It may be mentioned that FE-based devices have potential applications in flat panel display, microwave power amplifiers, electron microscopes as well as gas and mass sensors [57,64,65].

Among various field emitters, Si-based ones are extremely important for micro- and nano-electronics due to their low mass and volume with very low power requirements [66]. In addition, nowadays, Si-based field emitters are being used as neutralizers to reduce space craft charging which occurs as a side-effect during propulsion [67]. Hence, numerous studies have been directed towards the preparation of Si nanowires, nanobelts, nanoribbons, and nanotubes, and utilization of such nanostructures in miniaturized electronic devices which also show considerable FE property [68,69]. Si-based field emitters are fabricated by various catalyst or lithographic methods. For instance, silicon nanowires were grown on carbon cloth via the vapor-liquid-solid reaction using gold as catalyst which yielded a very low turn-on field of 0.7 V μm\(^{-1}\) [70]. On the other hand, Si nanotip array, formed by porous alumina mask, demonstrates a turn on field of 8.5 V μm\(^{-1}\) whereas for Si nanotubes, synthesized by template replication and chemical vapor deposition, the turn-on field value becomes 5.1 V μm\(^{-1}\) [71,72].

Although these results are exciting, such methods of fabrication have their own disadvantages, e.g. template-based lithographic techniques are expensive and template removal is difficult. On the other hand, in catalyst driven processes, metal particles may play the role of electron or hole traps in Si which leads to various contamination related problems [61]. This indicates that for commercial usage of Si as a field emitter, a single step large area fabrication process is required and those rely on self-organization of nanostructures are of special interest. However, under the exposure to ambient, these nanostructures are prone to get oxidized due to the formation of a native SiO\(_x\) layer (dielectric) at RT [73]. This creates an additional tunnelling barrier for electrons, resulting in a drastic reduction of the field emission properties. On the other hand, SiO\(_2\) is an important candidate in micro- and nano-electronics.
industry and helps Si surface to get rid of contamination related problems as well. Therefore, understanding the role of a native oxide layer in FE property of Si nanostructures is of utmost importance. In this context, it is a great challenge to develop a new method where Si nanostructures can be fabricated with a native oxide capping layer without much of a degradation in their FE property.

In the present study, we report on the FE from low energy ion-beam fabricated nanofaceted-Si structures [23]. Bulk measurements show an impressive turn-on field of 4.7 V µm⁻¹ and excellent stability. However, bulk FE bulk measurements cannot specifically identify the region of FE and hence, we have employed combined atomic force microscopy-based local tunnelling current and scanning Kelvin probe microscopy (SKPM) measurements to understand the local FE properties of such Si nanofacets. In fact, tunnelling current mapping conclusively shows that the valleys and the sidewalls of nanofaceted structures/nanofacets contribute more to the field emission process compared to their apexes. In addition, cross sectional transmission electron microscopy (XTEM) reveals that the apexes of the nanofacets are covered with native oxide whereas the side walls and valleys are crystalline. This presence of native oxide at apexes will increase the local work function and in turn reduce the electron tunnelling probability. This observation corroborates well with SKPM based studies.

5.2.2 Experimental

Silicon samples, used in the present experiments, were sliced out (1 × 1 cm²) from a p-type Si(100) wafer. A UHV-compatible experimental chamber, equipped with an electron cyclotron resonance based broad beam ion source, was used in this case. The chamber base pressure was below 5×10⁻⁹ mbar and the working pressure was maintained at 3×10⁻⁴ mbar. Samples were fixed on a sample holder which was covered by a sacrificial Si wafer (taken from the same lot of the substrate) to ensure a low impurity environment. Samples were exposed to 500 eV Ar-ions at an oblique incidence of 72.5° incidence angle (with respect to the surface normal) and
at an optimized fluence of $3 \times 10^{18}$ ions cm$^{-2}$ at RT. The beam diameter was measured to be 3 cm which corresponds to a fixed ion flux of $1.3 \times 10^{14}$ ions cm$^{-2}$ s$^{-1}$ (corresponding to a target current of 160 $\mu$A) in a plane normal to the ion-beam direction.

Surface morphology and local electrical properties of nanofaceted was examined ex-situ by atomic force microscopy in different modes using conductive tips (AC240TM, Electric-Lever, Olympus) and with a resonance frequency of 70 kHz. Further, dual pass tunnelling current microscopy (DPTCM) [equivalent to tunnelling atomic force microscopy (TUNA)] and SKPM studies were performed using a user-defined lift height of 20 nm from the surface [74]. It may be mentioned that AFM and SKPM measurements were accomplished with optimized drive amplitudes, frequencies, set points, and scan speeds. Moreover, AFM image analyses were carried out by employing WSxM and SPIP softwares [22,32]. In addition, microstructural study was performed by using high-resolution transmission electron microscopy (HRTEM).

Field emission measurements were carried out at RT in high vacuum ($3 \times 10^{-7}$ mbar) condition by using a two-electrode configuration with a copper anode and the sample was attached to the cathode plate with conductive copper tape (sheet resistance $\sim 0.004 \Omega/\square$). To ensure a stable emission, 10 cycles with external bias were applied before recording each data set.

### 5.2.3 Results and discussion

Figure 5.6(a) shows the current density as a function of the applied electric field for the Si nanofacets. The turn-on field (the field at which a sharp increment in current density is observed) was 4.7 V $\mu$m$^{-1}$. The pristine-Si did not show any emission up to 1000 V, (our measurement limit). The observed threshold emission is similar to the case of Si nanotube arrays where the value comes around 5.1 $\mu$m$^{-1}$ [72]. Fig. 5.6 (b) shows $1/E$ vs ln ($J/E^2$) plot which can be fitted linearly, indicating that FN mechanism is operative for the observed FE.

The enhancement factor, $\beta$, is calculated from the slopes of the fitted lines which turns out to
be ~1104, assuming the work function of nanofaceted-Si to be 4.8 eV [75]. We find that the enhancement factor turns out to be little low compared to the existing reports [71, 72] whereas the threshold field value is among the best reported ones in case of Si nanostructures.

Figure 5.6: (a) Field emission current density as a function of the applied electric field for the nanofaceted-Si (green) and pristine-Si nanotube (brown), (b) Fowler-Nordheim plot for the nanofacets. The straight line drawn is for guide to the eye.

The efficient field emission performance of nanostructured-Si is generally ascribed to the enhanced aspect ratio and sharp apexes of the structures. However, the bulk measurements cannot specifically identify the regions of a faceted structure which gives rise to FE. To overcome this problem, we employed AFM-based local probe technique to map the tunnelling current. In fact, tunnelling current is measured by using a dual pass technique [schematic shown in Fig. 5.7(a)] which is similar to the tunnelling atomic force microscopy (TUNA) process reported by Chatterjee et al. [74].

Advances in scanning tunnelling microscopy (STM) and AFM over the past few years have seen the development of this conducting-AFM/STM combination into a highly sensitive technique called tunnelling current microscopy [74]. This allows a tunnelling current to be obtained from a sharpened tip attached to a cantilever, while simultaneously the tip traverses across the sample surface tracking height and morphological information. Whilst standard STM requires sample surfaces to be smooth on the nanometer scale, the physical tracking of topography in tunnelling current microscopy means that samples with a surface rms roughness...
of several microns can be investigated over scan areas up to hundreds of square microns. This allows a wider picture of the overall morphology to be obtained. Physical tracking also means that, unlike the constant-current mode of STM, the height data collected via deflection of the cantilever beam avoids possible artefacts introduced by variations in the conductivity of the sample surface. Here, for the present study, we call it dual pass tunnelling current microscopy (DPTCM) (details are described in chapter 3). Microstructural investigation was carried out by using cross sectional transmission electron microscopy (XTEM) on faceted substrates. Figure 5.7(b) depicts a high-resolution XTEM image of representative a faceted surface (formed at a lower fluence value of $5 \times 10^{17}$ ions cm$^{-2}$) which shows the clear presence of lattice fringes, indicating the formation of crystalline facets. A careful observation reveals the presence of amorphous patches (marked by yellow dashed lines) around the apex of the facets, albeit they are absent at the valleys, i.e. between two facets. These patches may result from the presence of mostly native oxides (as confirmed from the XPS study and discussed in the section 5.1.3). Fig. 5.7(c) shows the surface topography image recorded during tunnelling current measurements, which clearly shows the apexes and valleys of nanofacets. Several scans (from various places) with different scan directions were performed to confirm the true electron emission sites. Figure 5.7(d) shows one of the maps of tunnelling current (FE) which clearly indicates (shown by green lines) that the apexes are not actually contributing to the FE process (in contrary to the present notion), rather sidewalls and the valleys of nanofacets are the preferential sites [marked by blue and green lines in Figs. 5.7 (c) and (d)] for electron emission for a tip voltage of 10 V (maximum voltage limit of the used AFM). In order to confirm that the measured tunnelling current was a true reflection of the emission properties of the surface and not simply an artefact of surface topology, scans were repeated in four different directions to check that the data from each scan were all in good agreement. Thus, the local tunnelling current measurements indicate that higher tip voltage is required to tunnel the electron from
apexes. In fact, this result shows the presence of trap states at the apex in the form of native silicon oxide which may lead to the suppression of FE from the apexes as observed from Fig. 5.7(b).

Figure 5.7: (a) Schematic of the DPTCM measurement using dual pass mode. (b) XTEM image showing silicon facets fabricated by using 500 eV Ar-ions to the fluence of $5 \times 10^{17}$ cm$^{-2}$. The yellow lines depict the zones where native oxides are present. (c) Topographical image of nanofaceted-Si surface in contact mode. Corresponding height scale is 0 to 414 nm. (d) Map of tunnelling current measurements showing clear contrast difference in the valley and apex. Corresponding height scale is 0 to 60 pA. Blue and green lines in (c) and (d) are for guide to eyes.

It may be mentioned that the growth of oxide layer on Si nanostructures is of great importance although the mechanism of oxidation is not well understood till date. Presently, various reports exist where the oxidation of Si nanostructures has been addressed. For instance, Büttner et al. reported on the retarded oxidation of Si nanowires due to increased stress at the Si/SiO$_2$ interface [69]. This stress value depends on the curvature of the nanostructures. As mentioned by Büttner et al., due to smaller curvature of the surface, oxidation of planar Si is
faster and follows the common Deal-Grove theory [76,77], whereas for nanowires, the increased curvature of the surface leads to a retarded oxidation effect. In another note, experimental and simulation studies show that the rounded Si shapes that appear after oxidation are caused by stress induced reduction of oxide viscosity [80]. These reports clearly indicate that the oxidation of Si nanostructures can be significantly different compared to planar geometry. Thus, in the present work, the presence of native oxide only at the apexes may be attributed to the inhomogeneous strain and stress distribution for a non-planar geometry (leading to a different curvature compared to the planar geometry) of the nanofacets.

Generally, field emission, a quantum mechanical tunnelling of electrons, from the surface of a semiconductor depends on the work function of the materials. In the present case, the presence of native oxide at the apexes should influence the field emission mechanism. Thus, to understand the role of native oxide, we used scanning Kelvin probe microscopy (SKPM). In fact, SKPM measures the constant potential difference ($V_{CPD}$) between tip and sample which can be written as: $V_{CPD} = (\varphi_{tip} - \varphi_{sample})/q$, where $\varphi_{tip}$ and $\varphi_{sample}$ are the work functions of the tip and sample, respectively [79] while $q$ is the electronic charge. Thus, to find out the work function, SKPM measurements were carried out at various points of a particular nanofacet. Fig. 5.8(a) shows the topographic image of a Si nanofacet from which a clear difference in the height contrast at apex and valley is observed. On the other hand, Fig 5.8(b) shows the corresponding SKPM image. A clear difference in the contrast of the apex and the valleys is seen which actually signifies the spatial variation of the work function over the surface. However, due to inhomogeneous nature of the native oxide formed on Si nanofacets, this image cannot be converted directly into work function mapping. Thus, we measured $V_{CPD}$ values at different points of a single facet as shown in the topographic image for a better realization of the apex point and the valley [Fig. 5.8(a)] and correlate with the corresponding SKPM image. For instance, we found out the respective work functions values from the locations marked by
(i), (ii), (iii), and (iv). By taking into account the work function of the tip (Si coated with Pt/Ir) is \( \sim 4.85 \) eV [80], the measured work function at points (i), (ii), (iii), and (iv) are found to be 4.75, 4.78, 4.71, and 4.73 eV, respectively.

Figure 5.8: (a) topography image of a single nanofacet having a height scale of 101 nm. (b) SKPM image of nanofaceted-Si surface depicting variation of work function over the surface. Corresponding height scale is 70 to 120 mV. (i), (ii), (iii), and (iv) are the regions from where corresponding work functions are calculated.

It is observed that the nanofaceted-Si apex has higher work function (\( \sim 50 \) meV) compared to those of valleys [the difference between points (ii) and (iv) in the topography]. This is due to presence of native oxide layer at the apexes of the nanofacets. It may be mentioned that the work function of the apex shows a mismatch with respect to the pure SiO\(_2\) work function which may be due to its very low thickness [81]. Thus, SKPM measurements further supports the observation of suppression of field emission from the apexes of the nanofacets due to high degree of variation in the work function values from apex to valleys.

5.2.4 Conclusions
In conclusion, the possibility of using self-assembled nanofaceted-Si substrates as stable field emission cathodes has been demonstrated. It has been shown that these Si nanofacets yield an impressive turn on field of 4.7 V/\( \mu \)m. Local probe based DPTCM technique unfolds that the
valleys and the sidewalls of nanofaceted-Si contribute more to the field emission process compared to the apexes. This can be attributed to the formation of a native oxide layer at the apex of the facets. The presence of native oxide at the apexes may result from the inhomogeneous stress distribution over nonplanar geometry. This corroborates well with the XTEM and SKPM studies. Actually, native oxide layer leads to the variation in the work function from tip to the valley of the facets, observed from the SKPM measurements, causing a suppression of the electron emission from the apexes. Our experimental findings demonstrate a novel way to address the field emission in a very local scale by using local probe based microscopic techniques.

Bibliography


