Synopsis

Nowadays, cutting edge research requires tailor-made properties of materials for advanced technological applications. In the context of synthesis and modification of physical (e.g. structural, optical, and magnetic) properties of materials in micro- and/or nano-scale, ion irradiation offers a precise control to achieve the same. Ion bombardment is a non-equilibrium processing route which offers deposition of energy in a target material, leading to radiation damage, introduction of foreign atoms into the target beyond equilibrium thermodynamics in the form of ion implantation, and also removal of surface atoms of the target known as sputtering. Recently, a lot of effort has been put to make use of ion-beam sputtering in creating self-organized patterns on materials surfaces.

Fabrication of semiconductor nanostructures in a controlled manner is one of the key requirements for developing optoelectronic devices. Although electron-beam lithography is able to the fabricate nanoscale structures, the low throughput of serial lithographic methods and high production cost pose severe problems. Thus, a constant effort is being put to look for smart techniques to generate surface nanostructures. Ion beam sputtering is commonly employed in many industrial processes to modify the properties of solid surfaces. Under certain experimental conditions, the bombardment of solid surfaces by low and medium energy ions may induce a surface instability that results in the formation of periodic patterns with nanometer periodicity on irradiated surfaces [1]. Depending on the irradiation conditions, different nanoscale patterns can evolve in the form of periodic ripple patterns, hexagonally ordered dot arrays, and faceted structures [2], with periodicities ranging from few tens to several hundreds of nanometres. Over the years, sputter-induced ripple structures were observed in different materials like insulators, semiconductors, and metals [1].
For last two or three decades continuous effort is being made to explain evolution of solid surface topography during ion-beam irradiation. It started with the notion that pattern formation is usually governed by an interplay between the dynamics of surface roughening due to sputtering and smoothing due to material transport during surface diffusion. Models have shown that surface instabilities can arise from curvature-dependent sputter erosion or due to ion impact-induced mass redistribution. The first successful continuum theory to explain ripple formation was developed by Bradley and Harper (BH) on the basis of so called micro-roughening instabilities [3]. By using Sigmund’s theory [4] of sputtering, they were able to show that the curvature-dependent sputtering yield induces an instability at the surface which leads to an amplification of initial modulation. Under the presence of smoothening process like surface self-diffusion, a wavelength selection is observed. BH theory is able to reproduce early stage of ripple evolution and ripple rotation albeit the presence of a stable surface up to a critical angle of incidence in case of monatomic materials (e.g. Si and Ge) remained unsolved. In another note, the smoothing at angles below the critical angle was addressed by Carter and Vishnyakov (CV) [5]. These two effects, viz. BH and CV have been combined into a single framework by Madi et al. where they have clearly enunciated that it was actually the prompt atomic redistribution (rephrased CV effect) as compared to sputter erosion which governs the pattern formation on Si under ion bombardment and explained the presence of a stable surface below the critical angle as well [6].

On the other hand, an alternative model known as hydrodynamic approach, also describes low energy ion induced pattern formation. It, basically, deals with the idea of amorphous solid flowing due to ion impact at a proper time scale. A small extension of this approach is the solid flow model [7] where ion-induced stress eventually drives the solid to flow with the pre-amorphized layer generated due to ion bombardment and as a result surface nanopattern develops. Solid flow model offers the advantage of time dependent (dynamic) evolution of
ripple patterns at a timescale where molecular dynamics (MD) based calculations cannot probe properly. In fact, this is the first theory to predict the timescale (intrinsic timescale) beyond which nonlinear effect starts appearing in the system. Although BH theory explains early stage of ripple evolution, the saturation of ripple amplitude at a longer timescale cannot be explained within the framework of a linear continuum model. In the nonlinear regime, surface roughness does not follow the exponential behaviour and ripple coarsening may take place [8]. Cuerno and Barabási developed a nonlinear continuum equation of Kuramoto-Shivashinsky (KS)-type [8]. It is to be noted that apart from nonlinear effects, the role of shadowing becomes crucial in pattern formation, particularly at higher oblique angles of incidence. According to Carter, due to shadowing of the incoming ion-beam, ripple structures can be transformed into triangular faceted structures [9]. However, this shadowing transition and the role of sputtering for the same are not well documented [especially in the low energy (few hundreds of eV) regime] till date. Thus, systematic experimental studies at higher oblique incidences are required to understand the underlying mechanisms, governing the pattern formation. These may be achieved by studying the temporal evolution of nanopatterns at grazing incidences where one can expect faceted/sawtooth morphology.

Apart from studying the fundamental aspects of pattern formation, nowadays, ion-induced nanopatterns become interesting for various technological applications. Experiments reveal the applicability of nanoripples in fabrication of optically active and electronic devices. Very recently, Martella et al. [10] reported on the broadband light trapping property of self-organized nanopatterned Si substrates which can be effectively used for photon harvesting in ultra-thin crystalline solar cells. In addition, rippled substrates are becoming potential templates for thin film deposition. For instance, Ranjan et al. [11] showed silver nanoparticles on Si ripples are capable of tuning the plasmon resonance while recently, tunability of magnetic anisotropy in Fe/Cr/Fe multilayer structures was demonstrated by Körner et al. [12] by using nanoscale
rippled Si templates for depositing. All the above-mentioned studies indicate the multifaceted applications of patterned substrates where they themselves or in the form of a template leads to modification of optical, photovoltaic, and magnetic properties of the materials.

For technological purpose, it is necessary to have a precise control over the patterns. This, in turn, requires detail knowledge of the pattern formation process and the underlying mechanisms. Different theories are emerging to explain the observed patterns which are accompanied by a large number of experimental data. However, the field is suffering from various issues like impurity induced pattern formation and the lack of lab-to-lab reproducibility. This indicates, up to now, the pattern formation mechanism is not fully understood. Thus, it is exigent to first optimize the pattern formation process and then explore the possible technological applications. In fact, systematic experimentation is needed to understand the role of sputtering, shadowing (at higher oblique incidences), and concurrent substrate rotation in pattern formation. The next step would be to use those patterns for some application purpose.

The second aspect is related to the application of the above-mentioned nanostructures where we have used rippled- and faceted-Si as templates for deposition of Al-doped zinc oxide (AZO) thin films which is known to be a transparent conducting oxide. The conformal growth of AZO overlayer was studied for both rippled- and faceted-Si. For rippled-Si substrates, a thickness-dependent shift in the excitonic peak of AZO was observed from the photoluminescence spectra which indicate the presence of quantum confinement effect. On the other hand, AZO on faceted-Si showed tunable antireflection property with varying AZO thickness. Moreover, AZO/faceted-Si heterojunction showed enhanced solar cell efficiency and spectral response.

Pulsed dc magnetron sputtering setup. To analyse the morphology, microstructure, composition, and crystallinity of the samples we used atomic force microscopy (AFM), scanning electron microscopy (SEM), cross-sectional transmission electron microscopy
(XTEM), energy dispersive X-ray spectrometry (EDS), X-ray photoelectron spectroscopy (XPS), and X-ray diffraction (XRD), respectively. In parallel, simulations of ion-solid interaction were performed using SRIM and TRIDYN codes. The optical properties of nanofaceted-Si and AZO grown on faceted-Si were investigated using UV-Vis spectroscopy and photoluminescence. Finally, the optoelectronic properties of AZO/Si heterojunctions thin films were studied by I-V, C-V, and photoresponsivity measurements.

The thesis is organized in seven chapters. The first chapter provides a brief introduction, the second chapter describes the experimental techniques used in this thesis, and the third chapter provides the theoretical background of ion-beam induced pattern formation. In chapter 4, the experimental results are presented where we describe pattern formation in the angular window of 0°-85°. The presence of stable surface up to 50° (explained by CV effect) is observed whereas ripple formation start taking place from 51°. The temporal evolution of ripple morphology in the angular window of 51°-72.5° and its explanation in light of solid flow model. With the help of this model, we could also identify the linear and nonlinear regimes of ripple evolution. In addition, for the same angular window and beyond (up to 85°), we describe the pattern evolution in nonlinear regime. The present experiments show that beyond linear regime, with increasing ion incidence angle, coarsened ripple patterns (with wave vector oriented parallel to the direction of the ion-beam) are observed at 67°. Above this angle, a gamut of unusual patterns form (e.g. mounds, facets, and needle-like structures) before ripple rotation takes place (from parallel to perpendicular-mode) at 80°. It has been shown that the temporal evolution of morphology at higher oblique incidences (70°-72.5°) originates from the shadowing effect of the ion-beam, leading the ripples to get transformed faceted structures. At even higher fluences, coarsening of these facets are seen which is explained on the model proposed by Hauffe [13]. On the other hand, ripple rotation is explained in light of BH theory. It may be mentioned that beyond ripple rotation, we observe flat surface which is mostly attributed to low sputtering
yield and high degree of reflection of incident ions at grazing incidence angles. We have also shown the effect of concurrent substrate rotation on pattern formation in Si. It is observed that the stable surface remains stable while rippled and faceted surfaces get changed into mound-like structures. Corresponding temporal evolution study at a fixed angle of incidence ($67^\circ$) revealed coarsening of mounds. In addition, for a fixed angle of incidence of ion-beam, rotation speed variation leads to saturation of surface roughness. All these observations has been explained by a nonlinear theory proposed by Bradley [14].

In chapter 5, we show that faceted structures are capable of showing tunable antireflection, photoluminescence, and field emission properties. Photoluminescence property is attributed to various defects and surface states present in facets whereas the improved antireflection property (in the range of 300-800 nm) is attributed to the graded refractive index effect. In fact, it is evident that higher antireflection leads to an enhancement of photoluminescence intensity up to two orders of magnitude.

Such nanofacets could be potentially useful as electron emitters where the field lines should concentrate at the apexes reducing the barrier for electron emission. It may be mentioned that although Si nanowires/nanocones are likely candidates for potentially good field emitters the limitation comes due to surface oxidation of Si nanostructures. In this thesis, we have undertaken the case study of field emission from such self-organized faceted nanostructures. In doing so, we have used both bulk and local probe techniques. Bulk measurements indicate a turn-on potential of 4.7 Volt $\mu$m$^{-1}$ having a stability up to 1 h. However, bulk measurements cannot specifically identify the regions of faceted structures which give rise to field emission. To overcome this problem, we employed atomic force microscope-based local probe technique, namely tunnelling atomic force microscopy (TUNA) [15]. TUNA measurements clearly show that the sidewalls of Si faceted nanostructures actually contribute to the field emission process instead of the apexes. This observation can be explained in light of native oxide formation at
the apexes of the facets which corroborates well with transmission electron microscopy and scanning Kelvin probe microscopy based studies.

In chapter 6, we make use of nanostructured Si as templates for growth of ZnO:Al (AZO) thin films. At first, we show the conformal growth of AZO overlayer on rippled-Si and modification and tuning its optical property as a function of fluence. The role of quantum confinement has been highlighted to explain the observed blue shift in the near band excitonic peak. Next, we show the efficacy of AZO overlayers (30-90 nm) grown on ion-beam synthesized nanofaceted-Si for further suppressing the reflection down to very low values. In particular, we observe tunable antireflection property from conformally grown AZO layers, followed by a systematic shift in the reflection minima from ultraviolet to visible to near-infrared regions with increasing thickness. Tunable antireflection property is understood in light of depth-dependent refractive index of nanofaceted-Si and the AZO overlayers. The antireflection property helps increasing the fill factor of such textured AZO/Si heterostructure, which reaches its maximum for 60 nm AZO compared to the ones based on planar-Si. This thickness matches with the one that shows the maximum reduction in surface reflectance. In order to understand the decrease in the fill factor at higher AZO thicknesses (>60 nm), current-voltage (I-V) and capacitance-voltage (C-V) measurements were carried out. I-V measurements reveals increase in the leakage current beyond 60 nm thick AZO which in turn reduces the fill factor. However, thickness-dependent enhancement in the photoresponsivity is attributed to the reduced potential barrier across the $n$-AZO/$p$-Si junction due to the use of nanofaceted-Si templates as corroborated from the capacitance-voltage measurements.

In chapter 7, we provide a summary of this work which deals with low energy ion-beam induced self-organized nanopatterning of $p$-Si(100) surfaces. In order to do so, a large angular window (0°-85°) and energy in the range of 500-1750 eV were chosen. The experimental studies show the presence of stable surfaces up to 50° whereas surfaces become unstable in the angular
window of 51°-80°. In the linear regime, ripple evolution is explained by solid flow model, whereas ripples get coarsened in the nonlinear regime. In addition, at higher oblique incidences (70°-72.5°), ripple-to-facet transition has been demonstrated due to shadowing effect. The coarsening behaviour of the observed facets as a function of time at higher oblique incidences is attributed to the reflection of primary ions from the neighbouring facets. These ion-beam fabricated faceted nanostructures are seen to be capable of showing tunable antireflection, photoluminescence, and field emission. From the application point of view, the ion-beam fabricated rippled-Si substrates are demonstrated to be useful in modifying photoluminescence of AZO overlayer. On the other hand, upon using nanofaceted-Si as templates, for conformal growth of AZO, we show tunable antireflection and photovoltaic properties. The tunable antireflection due to the underlying nanofaceted-Si substrates leads to an enhancement in the fill factor (maximum for 60 nm thick AZO overlayer) of AZO/faceted-Si heterojunction solar cell by a factor of 2.5. In addition, concurrent substrate rotation during ion bombardment yields formation of mounds at those incidence angles where we observe ripples and facets in the static case. In this chapter, we also provide a scope of future work in this direction.

Bibliography