Chapter 8

Summary and Conclusions

This flag is of Indian Independence! Behold, it is born! ....
.... I call upon you, gentlemen to rise and salute this flag of Indian Independence.

- Madam Bhikaji Cama, Stuttgart, Germany, August 22, 1907

The work presented in this thesis deals with the growth of self-assembled semiconductor and metal nanostructures on atomically clean silicon surfaces as well as the growth of semiconductor nanostructures on oxidized silicon surfaces using molecular beam epitaxy (MBE). MBE growth provides atomic-scale sharp interfaces between the nanostructure and the substrate surface. Most of the nanostructures were epitaxially grown on atomically clean single crystal [low-index such as (100), (110) and (111)] surfaces of Si substrates. Clean Si surfaces show surface reconstruction, i.e. rearrangement of atomic positions on the surface leading to a unit cell different from an ideal surface. Surfaces of some orientations, even without any deposited material, show the formation of nanostructures because of reconstruction. For example, Si(110) surface with a (16×2) reconstruction show a nanowire-like structure. Studies on this surface and adsorption of metal atoms on this surface with the associated evolution of electronic structure have been presented. It is important to understand this initial stage of growth for an understanding of epitaxial growth of nanostructures. Different techniques have been used for various characterizations purpose. In
order to study the morphology of the clean surfaces and grown nanostructures, we have mainly used *in-situ* scanning tunneling microscopy (STM) and *ex-situ* high resolution transmission electron microscopy (HRXTEM). Electronic structure and the local density of states (LDOS) have been investigated by *in-situ* scanning tunneling spectroscopy (STS) measurements. X-ray diffraction (XRD) and grazing incidence X-ray diffraction (GIXRD) studies have been made to understand the lattice orientation and tilt present in the nanostructures. Growth and *in-situ* experiments were carried out under ultrahigh vacuum (UHV) condition. Growth on nanostructures on fractal surfaces may provide modification of electronic structure of nanostructures. The role of ion beam irradiation of substrates to produce fractal surfaces or modify fractal dimension is well known. An investigation on the determination of threshold fluence to make a Si surface self-affine fractal by ion bombardment is presented.

It is very important to prepare an atomically clean substrate surface on which an epitaxial layer or lower dimensional structures are to be grown. Thermal treatment under UHV condition is a standard procedure to prepare such clean surfaces by which the native oxide layer from a silicon surface is removed and the clean reconstructed silicon surface is prepared. Si(100) and Si(111) surfaces usually show \((2 \times 1)\) and \((7 \times 7)\) surface reconstructions, respectively whereas a Si(110) surface shows a wide variety of surface reconstructions. Among them \((16 \times 2)\) and \((5 \times 1)\) are considered to be the two primary reconstructions for Si(110) surfaces. Some reconstructions are only observed for ultraclean surfaces and therefore these reconstructions are the signature of cleanliness of a surface. The cleanliness of the surfaces are confirmed by RHEED and STM measurements via the observation of the respective surface reconstructions in reciprocal and in real space respectively. This is the primary requirement before starting the growth. These aspects have been presented in details.

As an example of self-assembled growth of epitaxial nanostructures we have studied growth of Ge on clean Si(100)-\((2 \times 1)\) surfaces. This growth is a case of classic
Stranski-Krastanov (SK) or layer-plus-island growth. Initially Ge grows up to 3 mono-layer (ML) as layer-by-layer (called the wetting layer). Upon further deposition Ge starts forming islands to relax the strain developed in the layer due to 4.2% lattice mismatch between Ge and Si. During the growth it follows a rich sequence of different island shapes. Our STM and HRXTEM measurements confirmed these different shapes of the Ge islands. HRXTEM measurements done in the present study show that the small coherently strained islands are dislocation free, however, with an increased deposition (coverage) of Ge the island size becomes bigger and finally relaxed islands are formed by introducing misfit dislocations.

We have observed growth of very small pyramid- and dome-shaped Ge nanostructures on Si(100)-(2×1) surfaces. At a growth temperature of 550° C, which is relatively low especially for dome-shaped Ge island growth, and in the absence of post-deposition annealing we observe an abundant growth of Ge domes. This might be a consequence of the low deposition rate used in our experiment. A sizable number of these Ge islands have an aspect ratio of ~ diameter : height = 1:1. STM and HRXTEM images reveal the formation of very small pyramids, truncated pyramids, domes and large facetted domes in the film. Since STM and AFM techniques will not reveal a narrow contact region of the islands with the wetting layer, here we have used the HRXTEM technique, which reveals, for some Ge islands, the presence of a narrow contact region between Ge islands and the wetting layer. Dome-shaped small Ge islands with low aspect ratio, nearly hemispherical shape and a narrow neck contact with the wetting layer, as observed in the present study, are expected to be useful in tuning quantum states in Ge quantum dots. The confining potential barrier at the interface, and hence the energy levels, would depend on the contact area of the quantum dot with the wetting layer.

We have observed the growth of nearly spherical, self-assembled Ge islands with a narrow contact area with the substrate on air-exposed Si(111)-(7×7) surfaces. The exposure of a Si(111)-(7×7) surface to air leads to the growth of a thin (~ 1 nm)
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oxide on the surface. Depending on the growth conditions these Ge islands are found to be usually small, in some cases as small as $\sim 2$ nm diameter. At 520 °C growth temperature, we observe the formation of both epitaxial and nonepitaxial Ge islands. However, at 550 °C, the islands are found to be epitaxial and with a typical diameter $\leq 10$ nm. At an elevated growth temperature, voids are formed on the oxide layer of the Si surface via reaction of Ge adatoms with the silicon oxide. Epitaxial Ge islands then grow through the voids forming narrow-neck and in contact and epitaxy with the Si surface. On the other hand nonepitaxial Ge islands grow where the intact oxide layer prevents growth of Ge in contact with the Si lattice. A major fraction of Ge islands grown at 550 °C has an aspect ratio (diameter : height) in the range of 1:1–1:2, whereas standard self-assembled growth of Ge on clean Si surfaces yields islands of aspect ratios in the range, 5:1–10:1. Self-assembled islands grown on the air-exposed surface also have reasonably uniform size distribution as opposed to distinct bimodal size distribution observed for self-assembled growth on clean Si surfaces. The oxide layer between the Ge islands and Si offers an electron tunneling barrier for electron transport through these islands. A narrow contact of Ge islands with Si through the oxide layer would still offer a barrier, albeit smaller in comparison with the intact oxide. This gives rise to tunability of the electronic levels in Ge islands. The present work reveals the interesting result that even on the presumably dirty surface of air-exposed Si(111)-(7×7) surfaces, epitaxial Ge islands can be grown.

We have investigated the electronic structures of the Si(110)-(16×2) reconstructed surface and a low-coverage Ag-adsorbed Si(110)-(16×2) reconstructed surface by scanning tunneling spectroscopy. Electronic local density of states have been probed by the measurement of conductance. Local density of states on the nanowire-like stripes of Si on the (16×2) reconstructed bare Si(110) surface show a band gap comparable to that for bulk Si. Upon low coverage ($\frac{1}{3}$ ML) Ag adsorption at room temperature on this surface, LDOS, in general, show a wider band gap compared to bare surface. A variation of band gap has been observed when LDOS have been obtained from different spatial locations. In addition new electronic states appear within the band
gap. We also observe a general trend of band offset in the STS spectra taken at different locations on the Ag-adsorbed Si(110)-(16×2) surfaces. All these features are qualitatively explained by a one-dimensional tight binding model using Green's function formalism. Many features of similar problems can be investigated by this model. For example, the effect of various types of sequences in the dangling or side chains can be investigated. Though not investigated here, the effect of length disorder of the side chain on the spectra can also be investigated.

For room temperature Ag growth on clean Si(111)-(7×7) surfaces by molecular beam epitaxy (MBE), we observe a general trend of Ag islands growing with even-atomic-layer heights on top of a Ag wetting layer. Growth of Ag islands with odd-atomic-layer heights were found in much less abundance. An in-situ scanning tunneling spectroscopy (STS) study has been carried out on Ag islands of different heights grown on clean Si(111)-(7×7) surfaces. The spectroscopy results show a correlation between the preferred island height and the relative positions of the HOS and the LUS of Ag islands with respect to the bulk Fermi level. An attempt has been made to correlate the observed height preference of Ag islands grown on Si(111) surfaces with the relative position of the HOS and LUS of the island w.r.t the Fermi level (E_F) of the system. A general trend of shifting of the HOS bands towards lower energy side for even-atomic-layer height Ag structures was observed. This electronic energy lowering appears to be the reason for the stability of the islands containing an even number of Ag atomic layers in the island height. Origin of this height preference for an even number of Ag atomic layers in the islands has been explored by density functional theory calculations. Preliminary theoretical results appear to explain the height preference.

When Si surfaces are bombarded with 2 MeV Si⁺ ions at a fluence of 4×10¹⁵ ions/cm², smoothing is observed at smaller length scales while surface roughness remains practically unchanged at larger length scales. In the smoothed regions, typically of length scales < 50 nm, the surface roughness has a scaling behaviour in conformity with a
self-affine fractal surface. The observed roughness exponent $\alpha = 0.53$ corresponds to a local fractal dimension of 2.47. In order to study the evolution of surface smoothing as a function of ion fluence and identify the minimum threshold fluence for the formation of smoothed self-affine fractal surface, studies were conducted in the ion fluence ($\phi$) range $5 \times 10^{13} - 5 \times 10^{15}$ ions/cm$^2$. The threshold fluence for this process was found to be $\phi_{th} \sim 1 \times 10^{15}$ ions/cm$^2$. However, the roughness exponent observed in this study is $\alpha \approx 0.35$ in contrast to what was observed earlier ($\alpha = 0.53$). This discrepancy appears to have arisen from the different ion beam flux used in these two experiments.

The work presented in this thesis can be expanded in several directions. Difference in the electronic structure of Ag nanoislands depending on the island height, namely, whether an island contains an odd or an even number of Ag atomic layers, would give rise to reactivity with other atoms/molecules coming in contact. This would open up studies on quantum controlled chemistry. Epitaxial Ge nanoislands with an intervening oxide layer between Ge and Si or in narrow epitaxial contact with Si would provide an opportunity for studying the tunability of electronic states in the Ge islands, as the different cases provide a tunability of the potential barrier at the interface. Nanowire-like structure on the Si(110)-(16x2) surfaces can be further investigated by increasing the coverage of Ag deposition. It may be possible to obtain selective adsorption on the raised nanowire-like stripes, providing a periodic arrangement of Ag nanowires on Si.

"Cover mine eyes, O my Love!
Mine eyes that are weary of bliss
As of light that is poignant and strong
........................................
O shelter my soul from thy face!"

- Sarojini Naidu