Chapter 1

Introduction

Epitaxial metallic thin layers on semiconductor surfaces or buried under a shallow layer have attracted attention for both fundamental studies and applications in micro-electronic industries. These include three dimensional integrated circuits, novel devices such as metal base transistors and magnetic storing devices. Epitaxial growth provides sharp interfaces which are important for the fabrication of devices using ultrathin layers [1, 2].

Growth of epitaxial layers can occur in three different modes depending on the surface and interface energies (σ) of the overlayer and the substrate and their lattice misfit [3, 4]. The three growth modes are (a) Frank-van der Merwe (FM) or layer by layer growth (2D) [5], (b) Volmer-Weber (VW) or island growth (3D) [6] and (c) Stranski-Krastanov (SK) or layer-plus-island growth [7]. Growth of epitaxial layers/films can be homoepitaxial involving the same material or heteroepitaxial layers involving epilayers of different materials than the substrate. Two dimensional (FM) growth is preferred if energy difference Δσ is negative (Δσ = σ_f + σ_i - σ_s, where σ_f, σ_i, and σ_s are the free energies of the film, interface and substrate respectively). When Δσ is positive three dimensional (VW) growth is favoured. SK mode is in between these two growth modes — the epilayer starts to grow in the FM mode (Δσ < 0), after one or several atomic layers the relation in the energy balance changes, due to a strain, such that Δσ > 0 and 3D growth is preferred. The basic factors that determine these different growth modes are of elastic and electronic origin, i.e., (i) the
strain in the epilayer due to lattice mismatch between film and substrate (different lattice constants and/or different lattice structures) and (ii) the chemical bonding, between the adatom and the substrate. Both these factors influence the value of $\sigma$, Ideal layer-by-layer growth can occur, therefore, only in homoepitaxy. Heteroepitaxial growth produces strained epitaxial layers due to lattice mismatch between the substrate and the overlayer as they are different materials [8]. Strained epitaxial layers have interesting properties and are important in semiconductor devices [9]. Strained layers grow pseudomorphically up to a critical thickness beyond which there is a strain relaxation by introduction of misfit dislocations [10]. Also another interesting phenomenon occurs. In the SK mode, islands can undergo a shape transition as a mechanism for strain relief producing self-assembled quantum dot or quantum wire like structures [11]. In earlier studies in our laboratory this type of epitaxial growth of gold-silicide islands and their shape transition on silicon surfaces have been observed [12].

The growth features of epitaxial metallic layers on semiconductor surfaces strongly depend on the cleanliness of the metal-semiconductor interface, the diffusivity of the metal atoms in semiconductor and vice versa, the relative free energy of formation of various phases, growth temperature etc. Conventionally epitaxial layers on single crystal surfaces are grown under ultrahigh vacuum (UHV) conditions in order to avoid contamination. Under atmospheric or non-UHV conditions usually an oxide layer is easily formed on semiconductor surfaces. These oxide layers hinder epitaxial growth [13–15]. The oxide growth can be inhibited in some cases by passivation of the substrates via chemisorption of different elements. For example, the oxide growth on Si(111) substrates can be hindered by passivating the Si dangling bonds with Br by a chemical method [15–17]. This passivated Si surface has been used for metallic film (Cu, Au, Ag) deposition on them under high vacuum conditions. Recently the studies of growth on chemically bromine-passivated Si(111) (denoted hereafter by Br-Si(111)) surfaces have shown many interesting results. Thin Cu films deposited under high vacuum on Br-Si(111) surfaces showed interdiffusion behaviour across the interface similar to that for Cu films deposited under UHV condition on an atomically clean Si(111) (7 × 7) surface [14,15]. Epitaxial layers of Ag have been grown on Br-Si(111)
surfaces [18]

Au films deposited on Br-passivated Si(111) substrate under high vacuum, upon annealing around the Au-Si eutectic temperature (363 °C), showed several interesting features. These are growth of self-assembled epitaxial gold silicide islands over a uniform background in a layer-plus-island growth mode, island shape transition from triangular to trapezoidal islands, epitaxy driven fractal growths, etc [12,19,20] Many of the growth features are similar to those obtained in UHV experiments [21]

Also passivation of Si(110) surfaces with bromine has been possible [16,22] Growth of self-assembled long wire-like gold-silicide islands over a uniform background of silicide are observed on 363 °C-annealed Au/Br-Si(110) systems. The growth of long wire-like parallel islands with aspect ratio as large as 200:1 reflects the two-fold symmetry of the underlying Si(110) substrate [23] On a surface like Si(110) with a two-fold symmetry, anisotropic diffusion also contributes to the growth of wire-like structures [24] Although the passivation of Si(100) surface with Br is very short lived (less than an hour) [17], we have been able to grow square and rectangular shaped epitaxial gold-silicide islands on Si(100) surfaces, upon annealing the Au/Br-Si(100) samples around 363 °C Some additional studies of metal films on Br-Si(111) and Br-Si(110) surfaces and studies on Br-Si(100) surfaces are presented in this thesis

The shape and size of these epitaxial islands are controlled by the inherent properties of the systems, e.g., substrate surface symmetry, surface and interface energy, strain and defects. Thus the process is self-assembled. The self-assembling growth may provide a novel way of fabricating quantum dot and quantum wire structures

Thin films are most often grown away from thermodynamic equilibrium. In fact the degree to which the growth proceeds away from the equilibrium decides the extent to which morphology will be governed by the thermodynamic quantities like surface and interface free energies or by growth kinetics. In the present study, a number of strikingly new features in this heteroepitaxial island growth were observed with the growth of various hexagonal shaped islands on annealed Au/Br-Si(111) samples. What is more enigmatic is the fact that such remarkable changes in the shape and symmetry of the gold silicide islands were obtained by just varying the growth temperature by a narrow range around the Au-Si eutectic temperature (363 ± 30 °C)
A tentative comparison is given following Kinetic Monte Carlo (KMC) simulations results for similar systems. Some of the important aspects of these features mentioned above were reported in our earlier publications [12, 19, 20, 23]. Here, besides briefly summarizing some aspects of these epitaxial gold-silicide island growth in non-UHV conditions, some new results on these structures are presented.

For the study of micron sized self-assembled microstructures like those described above, we have developed an ion microbeam facility along with one of the beam lines of a 3MV Pelletron accelerator facility at our Institute. It has been demonstrated at various places all over the world [25, 26] that reducing the size of the probing ion beam to a few micrometers to sub-micrometers by properly collimating and focusing the accelerated MeV ion beam opens up the possibility of applications in a host of new systems in semiconductors (microelectronics), environmental, archeological and biological studies [25, 26]. Together with the ability of ion beam analysis to provide depth profiling, the ion micro-beam is indeed a very powerful tool to carry out materials analysis with the three dimensional imaging capability. A major portion of this thesis work include the development of this ion microbeam facility. Some of the results using this facility are presented.

Ag epitaxial layers on silicon single crystal surfaces, upon MeV Si ion irradiation, undergo improvement in crystalline quality. This is often associated with remarkable changes in surface morphology. Growth of micron sized (1 - 30 microns) islands has been observed on epitaxial Ag(111) thin films (~100 nm), deposited on Br-passivated Si(111) surfaces, when irradiated with energetic Si ions (1-12 MeV). This shows ion-beam-induced mass transport in the Ag layer. The islands on the surface of the Ag films, show a variation in height, diameter and number density as a function of ion energy as well as fluence. A detailed analysis with ion microbeam and atomic force microscopy is presented. Many islands interestingly appear to have a triplet pattern – the island, a depleted region around the island and a frozen wave packet. A tentative explanation for the formation of the triplet structure is given.

For studies on atomically clean surfaces, we have developed a ultrahigh vacuum (UHV) experimental set up involving sample cleaning and preparation of atomically
clean surfaces, monolayer level thin film(s) growth and studying various surface properties using diffraction of low energy electrons and Auger electron spectroscopy. The UHV set-up is connected with one of the beamlines of the 3 MV tandem accelerator facility to carry out ion scattering (RBS/channeling) measurements with MeV ion beams. The beam line and the details of the experimental set-up are described in this thesis. Some preliminary experimental results involving growth and characterization of Pb on Si(111) surfaces are presented.

In addition to the development of two beam lines of the 3 MV tandem ion accelerator and experimental facilities with them, this thesis deals with growth of Au, Ag and Pb layers on Si surfaces, growth of thermally or ion-irradiation induced self-assembled structures, epitaxial or otherwise, in these systems and characterization using ion scattering (Rutherford backscattering spectrometry and channeling), ion induced X-ray emission, Auger electron spectroscopy, optical microscopy and atomic force microscopy.

The thesis has been arranged in the following way. Following the introduction in this chapter, chapter 2 provides the theoretical background of the various characterization techniques we have used. With a brief descriptions of the 3MV pelletron accelerator facility at our Institute, the development of the ion micro beam facility is described in chapter 3. The studies of gold silicide on Br-passivated Si surfaces have been presented in chapter 4. Investigations of interactions of (2-12) MeV Si\(^+\) ions with Ag films on Br-Si(111) surfaces have been presented in chapter 5. The development of the surface physics beam line along with experimental facilities are described in Chapter 6. Some of the demonstrative experiments are also presented in this chapter. Finally chapter 7 presents the summary and conclusions.
Bibliography


Introduction


