Chapter III: Morphology and structure of ion beam sputter deposited metal thin films

Abstract

This chapter presents the study of microstructure and structure of single layer Ag and Au thin films by Ion Beam Sputter Deposition (IBSD) with argon ion energy in the range of 150 to 450 eV and beam current of 4 – 6 mA. The films were grown at temperatures from 30 to 300°C. It is shown that IBSD offers better controls over parameters for deposition of fine uniform thin films with controlled microstructure as compare to other physical vapour deposition techniques like DC sputtering and thermal evaporation. IBSD can be used as a non-lithographic technique to deposit self assembled/ordered nanostructured thin films. Different variety of nanostructures including self organized arrays of nanoparticles, nanoclusters and nanoneedles have been achieved. The coalescence behaviour of grown films are discussed and explained using known theory of growth mechanism of the thin films.
Chapter III: Morphology and Structure of ion beam sputter deposited metal thin films

3. Introduction

Recently, research on nanostructured metals has attracted much attention due to their applications in plasmonics and photonics. Two approaches are normally followed to achieve nanostructures in thin film form. The first set of techniques is based on lithographic techniques such as electron beam lithography, nanoimprint technology etc. [1, 2]. The second set of techniques is based on non-lithographic and direct writing methods such as focused ion beam, dip pen lithography, laser shock processing, electric field induced nanostructuring etc. [3, 4] Both these sets of approaches are post-processing methods that achieve nanostructures after a film is deposited on a substrate.

A third approach that has been successfully used for realizing a wide range of nanostructures are those based on soft chemical processes leading to self-organized, self-ordered and self-assembled nanostructures [5-8]. However, studies on the use of Physical vapour deposition (PVD) techniques to fabricate such structures are sparse [9, 10].

There are generally four main steps in the evolution of thin films deposited on substrates by PVD [11]. These are nucleation, island growth, agglomeration and finally continuous film. The first two stages would lead to largely discontinuous thin films. The microstructure at these early stages of growth would be controlled by process parameters like rates of deposition and substrate temperature and most importantly the nature of the film-substrate interface. For constant temperature and rate of deposition the growth would entirely be dependent on the nature of film-substrate interface. This is the basic premise of the current work and it is demonstrated that interfacial nanostructuring is a simple approach to achieve a variety of nanostructures such as nanoclusters, nanoparticle arrays and nanoneedles.
3.1. Comparison of microstructures

As mentioned above, there are many deposition techniques like chemical as well as physical vapor deposition but in the current work, we have used Ion Beam Sputter deposition (IBSD) technique to deposit metal thin films. IBSD technique has independently controllable parameters which provide flexibility in the deposition of novel thin film materials. One of the unique characteristics of IBSD is the ability to deposit multi component or multilayered materials using a single ion source. Ion beam sputter deposition offers the advantages of conventional sputtering while operating at a lower pressure. A low operating pressure minimizes the problem of substrate heating and gaseous impurity incorporation in the growing film. To show the flexibility and quality of films that can be fabricated by IBSD, we compared the microstructures of metal films deposited by ion beam sputter deposition technique with thermal evaporation and general DC sputtering.

Figure 3.1 shows the example of microstructure of Ag films deposited by different physical vapor deposition techniques. In figure 3.1 (a) Ag film deposited by IBSD at an Ar ion energy of 600 eV shows a uniform, spherical and dense microstructure compared to the films deposited by DC magnetron sputtering (at 300 V and 100 mA) and thermal evaporation technique shown in figure 3.1(b) and (c), respectively. The thickness of the films shown in the AFM image is 30 ± 3 nm for all the three films. It is also observed that the grain sizes are much smaller in the case of ion beam sputter deposited films compared to the other two techniques. The observed behavior of microstructure by IBSD is due to its independently controllable parameters, which is not possible in the other two techniques as difficult as mentioned in previous chapter. Therefore, it is concluded that the IBSD technique can be used to prepare very thin continuous films with good microstructure and also semicontinuous nanostructured thin films.

Some examples of microstructure of different metals deposited by ion beam sputter deposition are shown in Fig.3.2.
Fig. 3.1. AFM images of Ag thin films deposited by (a) Ion beam sputter deposited at 600 eV ion energy for 30 minutes (b) DC magnetron sputtered and (c) thermal evaporation.
Fig. 3.2. AFM images deposited by IBSD at 550 eV argon ion energy of (a) Ag (b) Au (c) Cu and (d) Ni thin films and its corresponding 3D view.
The morphology shown in AFM images in figs 3.1 and 3.2 are all for films deposited at ion energy of > 500 eV.

3.2. Optimization of ion beam parameters

In order to fabricate nanostructured thin films, the films were deposited at ion energy < 500 eV and a systematic study was done to estimate the thickness of the films. A graph of typical variation in the rate of deposition as a function of ion energy is shown in fig.3.3. It is evident that the rate of deposition increases with increase in incident ion energy from 150 to 600 eV. In this optimization experiment, the total duration of deposition was maintained constant as 30 mins., at each energy. The rate of deposition was calculated by dividing the measured thickness of the films with the deposition time. The minimum rate of deposition achieved was 0.01 nm/s at an ion energy of 150 eV. At this ion energy, the films became discontinuous for deposition durations < 30 min. and therefore, measurement of thickness was not attempted for such films. For fixed incident ion energy, a linear dependence of thickness on duration of deposition was assumed and the thickness of the discontinuous films was thus estimated by simply multiplying the rate of deposition calculated earlier by the duration of deposition.

The evolution of morphology with increase in incident Argon ions energy is clearly seen in the AFM images displayed in Fig.3.4. For the same duration of deposition of 15 minutes, as the energy increases from 150 to 600 eV, the films are island-like at 150 eV and become continuous at 600 eV. There are two effects of increase in the incident ion energy. The first is an increase in rate of deposition and the second is the consequent increase in thickness for the same duration of deposition. i.e. the film deposited at an incident energy of 150 eV for 15 min, will have a thickness of ~9 nm grown at 0.01 nm/s whereas the film deposited at 600 eV will have a thickness of ~32 nm grown at 0.04 nm/s. In each case the corresponding roughness profiles are also shown. Very little correlation could be made between surface roughness and ion beam parameters.
Fig.3.3. Variation in rate of deposition as a function of ion energy.
Fig. 3.4. AFM images of Ag films deposited for 15 min at (a) 150 (c) 200 (e) 300 (g) 400 and (i) 600 eV and corresponding particle distance Vs height profiles are shown in (b), (d), (f), (h) and (j) respectively.
The combined effect, of the increase in rate of deposition and thickness, leads to the formation of a continuous film as the ion energy is increased. In addition, there is densification of the films as the ion energy is increased. The densification is accompanied by a decrease in particle sizes as a function of increasing ion energy as observed here. The particles size for the films deposited at 150 eV is measured to be 60-110 nm, at 200 eV it is 20-40 nm, at 300 eV particle size is 20-50, at 400 eV, it is measured to be 80-120 nm and at 600 eV, the particle size is measured to be 40-60 nm. It is clearly seen that initially the particle size is larger and then it becomes smaller with the increase of ion energy and at 400 eV it is much larger and at 600 eV it breaks down to 40-60 nm. It can be confirmed that at 400 eV ion energy, particle size reaches its critical size and breaks down to smaller with further increase of ion energy. It may be noted that with increase in energy there is an increase in thickness from 9 (at 150 eV) to 25 (at 400 eV) and finally 32 nm (at 600 eV).

In general, Physical Vapour deposition of continuous thin films onto substrates involves the following stages: nucleation, coalescence, island formation and finally continuous thin films. It has been demonstrated both theoretically and experimentally that at all stages of growth there is increase in the size of particles/aggregates/islands. The increase in size is dependent on process parameters such as rate of deposition and substrate as well as conditions on the substrate. It is observed that the above shown morphology is following the theories of thin film nucleation which are discussed below.

3.3. Theories of thin film nucleation: Kinetic processes in nucleation and growth
3.3.1. Nucleation rate:

The nucleation rate is a convenient synthesis of terms that describes how many nuclei of critical size form on a substrate per unit area, per unit time. Nuclei can grow through direct impingement of gas-phase atoms, but this is unlikely in the earliest stages of film formation when nuclei are spaced far apart. Instead, the rate at which critical nuclei grow depends on the rate at which adsorbed monomers (adatoms) attached to it.

The nucleation rate \( \frac{dN}{dt} \) is essentially proportional to the product of three terms, namely,

\[
N\cdot A \cdot \left( \frac{\text{nuclei}}{\text{cm}^2} \cdot s \right) = N^* A^* \left( \frac{\text{nuclei}}{\text{cm}^2} \cdot s \right)
\]

(3.1)
$N^*$ is the equilibrium concentration (per cm$^2$) of stable nuclei and $\bar{\Phi}$ is the rate at which atoms impinge (per cm$^2$-s) onto the nuclei of critical area $A^*$ (cm$^2$). Upon calculation, the final nucleation rate becomes,

$$\bar{\Phi} = 2\pi r^* a_0 \sin \theta \frac{P N_A}{(2\pi M R T)^2} n_s \exp \left( \frac{E_{\text{des}} - E_s - \Delta G^*}{k_B T} \right)$$

(3.2)

where, $\theta$ = contact or wetting angle,

$r^*$ = critical nucleus size,

$n_s$ = nucleation site density,

$E_{\text{des}}$ = the energy required to desorb it back into the vapor,

$E_s$ = the activation energy for surface diffusion.

$\Delta G^*$ = critical free energy, $a_0$ is adsorbed monomer jump distance and $M$ is mass of film material and $R$ is the impingement rate.

The nucleation rate is a very strong function of the nucleation energetics which are largely contained within the term $\Delta G^*$. A high nucleation rate encourages a fine-grained or even amorphous structure while a coarse-grained deposit develops from a low value of $\Delta G^*$.

3.3.2. Atomistic Models of the nucleation rate:

Atomistic theories of nucleation describe the role of individual atoms and associations of small numbers of atoms during the earliest stages of film formation. An important advance in the atomistic approach to nucleation was the theory proposed by Walton et al. [12] which treated clusters as macromolecules and applied concepts of statistical mechanics in describing them. They introduced the critical dissociation energy, $E_i^*$, defined to be that required to disintegrate a critical cluster containing $i$ atoms into $i$ separate adatoms. The critical concentration of clusters per unit area of size $i$, $N_i^*$, is given by,

$$\frac{N_i^*}{n_0} = \left( \frac{N_i}{n_0} \right)^{i^*} \exp \left( E_i^* / k_B T \right)$$

(3.3)

which expresses the chemical equilibrium between clusters and monomers. Here, $E_i^*$ may be viewed as the negative of a cluster formation energy, $n_0$ is the total density of
adsorption sites, and \(N_1\) is the monomer density. Lastly, the critical nucleation rate (\(\text{cm}^{-2}\cdot\text{s}^{-1}\)) emerges as,

\[
i^* = a_0^2 n_0 \left(\frac{v}{n_0v}\right)^i \exp \left(\frac{(i^*+1)E_{\text{des}}-E_1+E_{\text{ir}}}{k_BT}\right)
\]  

(3.4)

Compared to the previous equation 3.2, this has the advantages of expressing the nucleation rate in terms of measurable parameters rather than macroscopic quantities such as \(\Delta G^*, \gamma\) or \(\theta\). A thermally activated nucleation rate whose activation energy is dependent on the size of the critical nucleus is predicted by equation 3.4. This suggests the existence of critical temperatures where the nucleus size and orientation may undergo change. After the calculations,

\[
i = n_0v \exp \left(-\frac{E_{\text{des}}+E_2}{k_BT_{1\rightarrow2}}\right)
\]  

(3.5)

\(T_{1\rightarrow2}\) is temperature at which there is a transition from a one- to a two-atom nucleus.

### 3.3.3. Kinetic models of Nucleation:

Microscopic approaches to the modeling of nucleation processes have stressed the kinetic behavior of atoms and clusters containing a small number of atoms. Rate equations similar to those describing the kinetics of chemical reactions are used to express the time-dependent change of cluster densities in terms of the processes which occur on the substrate surface. It is appropriate to start with the fate of the mobile monomers. If coalescence is neglected, then

\[
\frac{dN_1}{dt} = -\frac{N_1}{\tau_s} - K_1N_1^2 - N_1 \sum_{i=2}^{\alpha} K_iN_i
\]  

(3.6)

Here, \(\tau_s\) is mean free residence time before adsorbed monomer reevaporation.

This equations states that the time rate of change of the monomer density is given by their incidence rate, minus their desorption rate, minus the rate at which two monomers
combine to form a dimer. The latter term follows second-order kinetics with a rate constant $K_i$. The last term represents the loss in monomer population due to their capture by larger clusters containing two or more atoms. The general form of rate equation for clusters of size $i$ is

$$\frac{dN_i}{dc} = K_{i-1}N_{i-1} - K_iN_iN_i$$

(3.7)

Where the first term on the right expresses their increase by attachment of monomers to smaller $i-1$ sized clusters, and the second term their decreases when they react with monomers to produce larger $i+1$ sized clusters. Transient as well as steady-state (i.e. where $dN_i / dt = 0$) solutions have been obtained for the foregoing rate equations for a variety of physical situations and for arbitrary values of $i$. They typically predicts that $N(t)$ increases with time, eventually saturating at the value $N_s$. Venables [13] has summarized nucleation behavior for cases where $i$ assumes any integer value. In general, the stable cluster density is given by,

$$N_s = An_0(n_0)^p \exp(E/k_BT)$$

(3.8)

where $A$ is a calculable dimensionless constant dependent on the substrate coverage. The parameters $p$ and $E$ have respectively yielded values for $i^*$ and the energies of desorption, diffusion, and cluster binding.

### 3.3.4. Cluster coalescence and depletion:

As previously mentioned, the density of stable nuclei increases with time upto some maximum level before decreasing because of coalescence phenomena. Growth and coalescence of nuclei are generally characterized by the following features:

1. A decrease in the total projected area of nuclei on the substrate occurs.
2. There is an increase in the height of the surviving clusters.
3. Nuclei with well-defined crystallographic facets sometimes become rounded.
4. The composite island generally reasserts a crystallographic shape with time.
5. When two islands of very different orientation coalesce, the final compound cluster assumes the crystallographic orientation of the larger island.
6. The coalescence process frequently appears to be liquid-like with islands merging and undergoing shape changes after the fashion of liquid droplet motion. This is specially true at elevated temperatures.

7. Prior to impact and union, clusters have been observed to migrate over the substrate surface in a process described as cluster-mobility coalescence. Several mass transport mechanisms have been proposed in order to account for these coalescence phenomena and they are discussed in turn.

3.3.4.1. Ostwald Ripening:

Prior to coalescence there is a collection of islands of varied size, and with time the larger ones grow or ripen at the expense of the smaller ones. The desire to minimize surface free energy of the island structure is the driving force. Consider two isolated islands of surface tension $\gamma$ of different size in close proximity. For simplicity, assume radii to be spherical with $r_1$ and $r_2$ and therefore the free energy (G) of a given island is $4\pi r_i^2 \gamma$ ($i = 1, 2$). The island contains a number of atoms $n_i$ given by $4\pi r_i^3 / 3\Omega$, where $\Omega$ is the atomic volume. Defining the free energy per atom $\mu_i$ or chemical potential as $\frac{dG}{dn_i}$, after substitution,

$$\mu_i = \frac{d(4\pi r_i^2 \gamma)}{d(4\pi r_i^3 / 3\Omega)} = \frac{8\pi r_i \gamma dr_i}{4\pi r_i^2 dr_i / \Omega} = \frac{2\gamma}{r_i} \tag{3.9}$$

In chemical thermodynamics the chemical potential is often associated with the so-called escaping tendency of atoms. Where $\mu$ is large the effective atomic concentration is large, forcing them to escape to where $\mu$ is small. Ostwald ripening processes never reach equilibrium during film growth.

3.3.4.2. Sintering:

Sintering is a coalescence mechanism involving islands in contact. In the case of sintering or coalescence of contacting sphere of radius $r$, theoretical calculations in the metallurgical literature [14] have shown that the sintering kinetics is given by

$$X^n / r^m = A(T)t. \tag{3.10}$$
Here $X$ is the neck radius, $A(T)$ is a temperature-dependent constant that varies with mass transport mechanism, $n$ and $m$ are constants, and $t$ is the time. Of the several mechanisms available for mass transport in films, the two most likely ones involve diffusion either through the bulk or via the surface of the islands. For bulk diffusion $n = 5$, $m = 2$, whereas for surface diffusion $n = 7$, $m = 3$. Typical thumbnail calculations show that surface diffusion dominates sintering. While surface energy and diffusion-controlled mass transport mechanisms undoubtedly influence liquid-like coalescence phenomena, sintering mechanisms are unable to explain the following:

1. Observed liquid-like coalescence of metals on substrates maintained at 77 K where atomic diffusion is expected to cease.
2. Widely varying stabilities of irregularly shaped necks, channels, and islands possessing high curvatures at some points.
3. The large range of times required to fill visually similar necks and channels.
4. Enhanced coalescence in the presence of an applied electric field in the substrate plane.

3.3.4.3. Cluster migration:

The last mechanism for coalescence considered deals with migration of clusters on the substrate surface. Coalescence occurs as a result of collisions between separate island-like crystallites (or droplets) as they execute random motion. Interestingly, the mobility of metal particles can be significantly altered in different gas ambient. Not only do the clusters translate, but they have been observed to rotate as well as even jump on each other and sometimes reseparate thereafter. Cluster migration has been observed in many systems, e.g., Ag and Au on MoS$_2$, Au and Pd on MgO and Ag and Pt on graphite in so-called conservative systems, i.e., where the mass of the deposit remains constant because further deposition from the vapor has ceased [15, 16].

The surface migration of a cap-shaped cluster with projected radius $r$ occurs with an effective diffusion coefficient $D(r)$ having units of cm$^2$ / s. The movement of peripheral cluster atoms, the fluctuations of areas and surface energies on different faces of equilibrium-shaped crystallites, and the glide of crystallite clusters aided by dislocation
motion are three models which show the dependence of D on r. In each case D(r) is given by an expression of the form [17],

\[ D(r) = \frac{B(T)}{r^s \exp \left( \frac{E_c}{k_B T} \right)} \]  

(3.11)

Where B(T) is a temperature-dependent constant and s is a number ranging from 1 to 3. The cluster migration is thermally activated with an energy E_c related to that for surface self-diffusion, and that it is more rapid the smaller the cluster.

### 3.3.4. Coalescence and grain size:

The formation of polycrystalline film, particularly terms such as nucleation, growth, and coalescence, has a familiar ring in the metallurgical literature of solid-state phase transformations. For example, a cold-worked metal matrix transforms by nucleation of recrystallized grains (islands) followed by growth, thus consuming the surrounding matrix so that there is less area available for new nuclei. During recrystallization one region will start ahead of others because of some favorable local composition, temperature, defect, or bias in the system. Then nucleation occurs elsewhere, and later somewhere else, while growth continues independently in regions of prior nucleation. The situation is much like rain droplets falling on a pond. Where rain impinges on the pond, surface wave nuclei are created. The circular ripples grow outward and begin to impinge on one another. When all of the prior untransformed matrix disappears by grain growth and impingement or coalescence, recrystallization is complete.

An important equation based on an analysis by Avrami [18] is useful in describing the kinetics of such transformations. For the case of film nucleation and growth in two dimensions where circular disk like nuclei grow, the form of the equation is

\[ f(t) = 1 - e^{-\left[ \frac{\pi}{\hat{G} t^{3/2}} \right]} \]  

(3.12)

Where f(t) is fractional amount of transformation and t is the time. Furthermore, (nuclei/cm²-s) and \( \hat{G} \) (cm/s) are the nucleation and linear growth rates respectively. As a function of log t, f(t) is small during what may be thought of as an initial incubation
period, then rises sharply when nucleation and growth rates overlap strongly, and finally saturates at $f = 1$. The Avrami equation strictly applies to closed systems transforming under conditions where there is no matter exchange with the surroundings. Inclusion of the adatom ring apparently extends the equations validity to open systems.

### 3.4. Morphology and structure on smooth substrate: Normal Coalescence

From the results presented in section 3.2, it is observed that the particles are large and isolated at very low ion energy deposition because surface mobility of the substrate is much larger than the material at that point due to which the film material freezes as soon as the material impinges on the substrate. It is confirmed that the deposition at very low rate and very low ion energy leads to the isolated and island kind nanostructured thin films. As given in the theory, there are four main steps in the evolution of thin films deposited by physical vapor deposition (PVD) technique. These are nucleation, island growth, agglomeration and finally continuous film. The first two stages would lead to largely discontinuous thin films. The microstructure at these early stages of growth would be controlled by process parameters like rates of deposition and substrate temperature. The film growth is controlled during the island formation stage, prior to the coalescence stage, leading to self ordered nanoparticle arrays with different sizes, shapes and interparticle separation.

Fig.3.5. (a) to (c) shows the morphology of the films deposited at 150 eV, for different deposition times or different thicknesses. As the thickness is increased from 6 to 18 nm, the films evolve from self-ordered nanostructures at 6 nm (Fig. 3.5.(a)) to semi-continuous films at 15nm (Fig. 3.5.(b)) and finally to almost continuous films at 18 nm (Fig. 3.5.(c)).

The AFM images clearly indicate that there is evolution in both shape as well as size of particles as a function of deposition parameters. The two parameters that have been controlled here are the rate of deposition (by controlling the incident ion energy at the target) and the thickness by fixing the duration of deposition time. The effect of increase in rate of deposition (fig.3.4) is to decrease the particle size, increase density of packing and thickness. On the other hand, the effect of increasing thickness (at a constant rate of
**Fig. 3.5.** AFM images of the Ag films deposited at Ar ion energy of 150 eV at total duration of deposition of (a) 10, (b) 15 and (c) 30 minutes.
deposition) is to change the shape of particles from ellipsoidal to elongated particle chains that finally break into a dense packed microstructure of small spherical particles (fig. 3.5).

Fig. 3.6. (a) – (c) shows the morphology of Au thin films deposited at 250 eV for different duration of time. The films were deposited for 10, 25 and 30 min at 250 eV of Ar ion energy. Here also, we observed that with the increase of deposition time or thickness, the films become denser and continuous as observed in the case of Ag thin films. The reason for depositing Au film at 250 eV ion energy is because the sputter yield of Au is much lower than that for Ag. Hence, no film deposition occurred at 150 eV in the case of Au even for duration of 40 min.

The process of film formation by vapour deposition techniques involves the transition of a solid source material into a vapour that condenses on impact with the substrate surface into a solid film (of the source material). It is clearly observed that the morphological evolution of films is therefore, profoundly influenced by conditions on the surface of the substrate and deposition parameters. In other words, the shape, size and spacing of particles are entirely dependent on accurate control of growth parameters such as pressure, temperature and rate of deposition. However, in the case of Au it is not consistent as in the case of Ag. It is due to the wettability of Au to the borosilicate glass substrate and the contact angle to the substrate.

The observed behaviour can be attributed to two factors namely: low rate of deposition and high contact angle to the substrate. To distinguish the contributions between each of these factors Au films were deposited on Carbon coated Cu grids (used for TEM) at the same beam energy. But it was found that the Au films did not exhibit any observable growth on carbon for energies up to 450 eV, clearly indicating that the interfacial energy dominated over the low rate of deposition. “Potato” shaped cluster of particles appeared when the films were deposited on carbon at an ion energy of 450 eV and for a duration of 25 min as shown in fig. 3.7(a). For comparison, the TEM image of an Ag film grown for 20 min directly onto carbon coated Cu grids at 150 eV is shown in fig. 3.7(b).

It is evident from this figure that Ag films have started nucleating as in the case of the films grown on the BSG substrates. It is observed that the Au films grown on BSG substrate and CCG are totally different. Au films grown on CCG has a boot shape kind of
Fig. 3.6. AFM images of the Au films deposited at Ar ion energy of 250 eV a total duration of deposition of (a) 10, (b) 25 and (c) 30 minutes.
Fig. 3.7. Transmission electron microscope images of (a) Au film deposited using an Ar ion energy of 450 eV for 25 min and (b) Ag film deposited using an Ar ion energy of 150 eV for 20
structures arranged themselves in array form. In both cases, Ag and Au deposited on carbon, the particles arrange themselves in the form of array with sizes between 5-20 nm. Therefore, it can be inferred that the interfacial energy of Au on BSG is lower than that for Au on carbon leading to the differences in growth on the two substrates. The high resolution TEM images displayed in figs.3.7.(a) and (b) and the selected area electron diffraction patterns shown in figs.3.7(c) and (d) for Au and Ag respectively indicate that the films are crystalline. It is observed that in both the substrates borosilicate glass and carbon coated Cu grid, the films are discontinuous and arranged in array form. The corresponding selected area diffraction pattern is shown in fig3.7(c) and (d) respectively.

To investigate the growth patterns on a scale larger than those available with AFM and TEM, the growth was also examined under a scanning electron microscope. The early stages of growth on BSG substrates for both Ag (150 eV 10 min) and Au (250 eV 20 min) are similar, as seen from figs 3.8(a) and (b), respectively. The microstructure consists of an organized array of nanoparticles, as seen in the AFM and TEM images. Interestingly, in both cases the formation of nanoneedles has also been observed, as shown in figs 3.8(c) and (d) respectively for Ag and Au. They are of 500nm in length with diameters of the order of 30-40 nm. Interestingly in the case of Ag, the nanoneedle formation follows the process of organization in to an array of nanoparticles while it precedes it in the case of Au. The difference in behaviour can be attributed to the differences in interfacial energies in the two cases.
Fig 3.8. Scanning electron microscope images of (a) Ag film deposited using an Ar ion energy of 150 eV for 30 min, (b) Au film deposited using an Ar ion energy of 250 eV for 20 min onto (c) Ag film deposited using an Ar ion energy of 150 eV for 20 min and, (d) Au film deposited using an Ar ion energy of 250 eV for 30 min onto BSG substrates.
3.5. Morphology and structure on rough substrate: Abnormal coalescence

So far we have demonstrated the growth of films on different substrates at ambient temperature without considering the roughness of the surface of the substrate. There have been some attempts to model the growth of thin films on rough substrates [19-21]. The main aim of such work has been to study conditions under which smoothening of a thin film deposited on rough substrate occurs and can be controlled. There have been a few reports of experimental work where substrate roughness has been used as a control parameter for thin film growth [22–26]. All the earlier reports focus mainly on roughness evolution in the initial stages of growth but not on the size of islands/particles that constitute the film.

In this part, we demonstrate that substrate roughness influences not only film roughness in the initial stages growth but also the island sizes leading to abnormal coalescence behavior. Discontinuous Ag and Au films were deposited by low energy Ion beam sputter deposition onto rough carbon coated Cu grids (used for Transmission Electron microscopy) and borosilicate glass substrates. The evolution of morphology was studied by transmission electron microscopy (TEM) as well as atomic force microscopy (AFM). The Ag films were deposited at Argon ion energy of 150 eV while the Au films were deposited at ion energy of 450 eV. Here, two sets of experiment are done. One set of experiments was carried out on Ag and Au by varying deposition temperature from room temperature to 200 and 300°C for a constant duration of 40 mins. Another set of experiments was carried out on Au at constant temperature 300°C but time was varied from 5 to 15 mins.

Fig.3.9. shows the typical bright field TEM images of Ag films deposited at various temperatures. Room temperature sputter deposited films are shown in fig.3.9(a), and the corresponding particle size distribution is shown in Fig.3.9(b) and deposition at temperature 200 and 300°C are shown in fig.3.9(c)-(d) – fig.3.9(e)-(f).

It is evident that these films are discontinuous and are comprised of spherical particles with a peak diameter of 15 nm. As we increase the deposition temperature to 200°C, it is evident from the micrographs shown in Fig.3.9(c) that these particles are still spherical in nature with absence of particles of size greater than 15 nm (Fig.3.9(d)). The peak in this
case occurs at ~ 12 nm. A further increase in substrate temperature to 300°C causes the particle size to become smaller with absence of particles greater than 12 nm size. The nanoparticle nature of the films is retained even at this temperature (fig.3.9(e) and (f)).

Fig.3.10 shows the bright field TEM images of the Au films deposited at various temperatures under a fixed deposition time of 25 minutes. It is observed that, in contrast to the Ag films, the Au films deposited at room temperatures have shown “boot-shaped” particles as shown in the micrograph Fig.3.10(a). Corresponding lattice fringes are shown in Fig.3.10(b). As we increase the deposition temperature to 200 °C, it is clear that these clusters break up into smaller particles that are ellipsoidal in shape (shown in Fig. 3.10(c)-(d)). At substrate temperature of 300°C, these particles change to spherical in shape as shown in the micrographs in Fig.3.10 (d)-(f). These gold particles remain crystalline at all temperatures studied here. The corresponding high resolution lattice fringes are best indexed with pure gold. It is very interesting that these gold nanoparticles exhibit (111) texture at all temperatures.

The following observations can be made from figs 3.9 and 3.10.

1. The gold films are less discontinuous than the silver films with lower island density.
2. At room temperature, the Ag nanoparticles are nearly spherical in shape with interparticle separation that is larger than the particle diameter.
3. The Au particles cluster together to form the boot-shaped aggregates. The number density of these aggregates is small and the separation is smaller than their size on average.
4. As substrate temperature increases, the size of particles, in Ag and that of aggregates in Au decreases. It appears that the number density decreases in Ag but remains constant in the case of Au.
5. Both films show crystallinity but Au exhibits a (111) texture at all temperatures.
6. The island density increases with increase in temperature from approximately 3 x10^{15}/m^2 ambient temperature to 1 x10^{16}/m^2 at 300°C, but the fragmentation is accompanied by decrease in inter-island distance.
Fig.3.9. TEM images of Ag films and corresponding grain size distribution curve deposited at Room temperature (a)-(b), at 200°C (c)-(d) and 300°C (e)-(f) for 40 min at 150 eV.
**Fig. 3.10.** TEM images of Au films and corresponding high resolution lattice fringes are shown, (a)–(b) at RT, (c)-(d) at 200 °C and (e)-(f) at 300 °C, for 25 min at 450 eV.
The effect of increasing duration of deposition on the microstructure of gold nanoparticles, at a fixed substrate temperature of 300°C is shown in Fig.3.11. It is evident from the micrographs that the nanoparticles in these films have mean grain size of 7-10 nm for a deposition time of 5 minutes as seen in the fig.3.11(a), which decreases to 3-5 nm for deposition time of 10 minutes (fig. 3.11(b)) and remains constant at that size for deposition time of 15 minutes (fig 3.11(c)). Here again the island density increases with increase in duration of deposition, but the fragmentation is accompanied by decrease in inter-island distance.

It is evident from these figures that in the initial stages of growth of the Ag and Au films there is a decrease in particles/island sizes that we term as “abnormal coalescence” referring to the fact that there is coalescence but the size of the aggregates decreases instead of increasing. To investigate the origin of this behavior, films were also grown on BSG substrates (placed next to the CCG substrates) under the same deposition conditions. The effect of changing the substrate from CCG to BSG on the coalescence behaviour of the Ag and Au films is presented here. During the same deposition run in which the films were deposited on CCG, films were also deposited on to BSG substrates. The microstructure was examined using an atomic force microscope so that the films do not have to be removed from the substrate and hence the role of the substrate is still evident. The AFM images of silver films deposited on to BSG substrates maintained at ambient temperature, 200 and 300°C, respectively are shown in fig.3.12.(a), (b) and (c) respectively. It is clear that, at all temperatures, the films are continuous and there is no evidence for islands. The mean particle size was between 40-60 nm.

The surface roughness of these films is plotted in fig.3.13. (a) to (c) and it is evident that the average surface roughness is of the order of 0.2 to 1.0nm and the peak to valley height is of the order of 2 nm in all three cases, with no specific dependence on substrate temperature. It may be noted that the rms roughness values were <1nm for BSG while it was between 20-25 nm for the CCG substrates.
Fig. 3.11. Bright field TEM images of Au films deposited at 300°C under various deposition time, (a) for 5 min (b) 10 min and (c) 15 min, at 450 eV.
Fig. 3.12. AFM images of Ag films deposited on BSG substrates at (a) room temperature, (b) 200 and (c) 300°C.

Fig. 3.13. Roughness profiles of the Ag films deposited on BSG substrates at (a) ambient, (b) 200 and (c) 300°C.
The morphological evolution of Au films deposited on BSG substrates is shown in fig.3.14. (a), (b) and (c) for substrate temperatures of ambient, 200 and 300°C, respectively. As in the case of Ag, the Au films are continuous even at ambient temperature and remain continuous at higher temperatures. At ambient temperature the particles are of the order of 20-40 nm in diameter which increases to 50 to 70 nm at higher temperatures indicate coarsening of the grains. The particles also acquire elongated shapes at higher temperatures. The surface roughness of these films is plotted in figs.3.15. (a) to (c) from which it can be inferred that the average surface roughness is of the order of 1-2 nm and the peak-to-valley height is of the order of 2-3 nm, as in the case of Ag films.

The microstructural evolution on BSG is in contrast to that observed for the Ag and Au films deposited on CCG substrates. Even at the lowest temperatures and thickness the films are continuous and do not exhibit any evidence of islands or particulate growth. In both cases there is coarsening of particles with increase in temperature without much change in the surface roughness.

Several patterns of morphological evolution emerge, based on the results presented in figs 3.9 to 3.15. The first of these relates to the differences arising out of the different film materials deposited on the same substrate. It is thus expected that the morphological evolution of Ag on CCG will be different from that of Au on CCG and similarly on BSG. On both substrates Ag particles are more spherical than the Au particles that grow in the form of elongated ellipsoidal shapes. This difference can be explained using the free energy balance equation leading to Volmer-Weber type of growth [27-32].
Fig. 3.14. AFM images of Ag films deposited on BSG substrates at (a) room temperature, (b) 200 and (c) 300°C.

Fig. 3.15. Roughness profiles of the Au films deposited on BSG substrates at (a) room temperature, (b) 200 and (c) 300°C.
Three types of growth modes are observed, in general, for thin films deposited on substrates. These modes of growth named, Stranski-Krastanov, Volmer-Weber and Van der Merwe, originate from the free energy balance between the free energies of the substrate surface $\gamma_s$, the free energy of the film surface, $\gamma_f$, and the interface between the film and substrate $\gamma_i$. In addition to these contributions the contact angle $\theta$ between the film and substrate is also very important. The free energy balance can be expressed as

$$\gamma_s = \gamma_f + \gamma_i \cos \theta$$  \hspace{1cm} (3.13)

Some materials have a negative enthalpy of mixing with one another—they are miscible. These materials tend to mix strongly at the film substrate interface to give a film-substrate "interface width" that may extend over many atomic layers. Volmer-Weber type of growth leads to 3D islands since the film does not "wet" the substrate and the "interface width" of the growing surface increases with time.

This is manifested in eqn.(3.13) in the term $\cos \theta$ which defines the strength of the contribution of the vapour-solid contact angle to the growth of the film. It is evident from the microstructural evidence presented that the contact angle of Au is smaller than that for Ag on both CCG and BSG. For large contact angles the interface contribution dominates over that of the film surface free energy. Small contact angles also translate into better wettability of the substrate by the film material. Thus, wettability of Au on these surfaces is higher leading to elongated ellipsoidal shapes. The Ag-CCG/BSG contact angle is higher leading to more spherical shaped particles.

At a temperature, $T$, the growth of film is characterized by the diffusivity of adatoms, $D_a$ on the substrate surface. It is known that the $D_a$ has an exponential dependence on temperature that can be expressed as

$$D_a = D_s \exp \left(-\frac{E_a}{kT}\right)$$  \hspace{1cm} (3.14)

Where $D_s$ is a pre-exponential factor and $E_a$ is the activation energy for surface diffusion. The average grain size at impingement, $r_i$, is defined as

$$r_i = \left(\frac{A}{\pi}\right)^{1/2}$$  \hspace{1cm} (3.15)
where $A$ is the average in-plane area which depends on the relative rates of island nucleation and growth. The growth rate is also dependent on the distance, $\delta$, over which atoms adsorbed on the substrate surface can diffuse to a growing island. This, in turn, depends on the adatom diffusivity on the substrate surface, $D_a$. Once islands have coalesced, further film thickening generally occurs by further growth of existing crystals rather than nucleation of new islands.

The increase in particle/grain size of Ag and Au films on BSG substrates follows the normal pattern of coarsening expected, as a function of increasing thickness and temperature.

The models discussed above successfully describe the growth of thin films on smooth, flat and planar substrates and the behaviour is referred to (in this work) as “normal coalescence”. Normal coalescence indicates grain coarsening as a function of increasing temperature and thickness of films, in the early stages of growth. These models, however, do not take into account the roughness of substrates and are therefore unable to predict its effect on film growth. The effect of substrate roughness on the roughness of films grown on such surfaces has been reported by a few workers. Anders et al. [22] have investigated nucleation and coalescence of silver islands on glass by in situ measurements of the sheet resistance. Sub monolayer amounts of niobium and other transition metals were deposited prior to the deposition of silver. It was found that in some cases, the transition metals lead to coalescence of silver at nominally thinner films with smoother topology. The smoothing or roughening effects by the presence of the transition metal was explained by kinetically limited transition metal islands growth and oxidation, followed by defect dominated nucleation of silver. Gyure et al. [23] presented experimental data for the morphological evolution of InAs buffer layers which are interpreted using continuum equations of motion and kinetic Monte Carlo simulations. They observe the formation of mounds in the early stages of growth and the presence of an instability even as an initially rough surface smoothen during growth. This instability is claimed to be due to the step-edge barrier which causes a characteristic length to emerge while the surface roughness is decreasing, well before the formation of the mounds. Coluci and Cotta [24] have carried out a similar Monte Carlo simulation of the morphology evolution of films grown on rough substrates. The surfaces considered for the simulation are similar to those of substrates used for the growth of GaAs films by chemical and molecular beam epitaxy.
When the growth is simulated, decreasing film roughness is observed until a stable value is reached. During this decrease the formation of mound like structures of a few monolayers in height was observed. In some conditions the structures forming the initial rough surface present a limitation to the lateral size of these mounds. Significantly, their study predicts a surface roughness dependent size limitation but it has not been quantified. Another significant work was reported by Mathur and Erlebacher [25] who investigated the growth of thin (1–10 nm) films of Pt on Au(111). It was found that on flat Au(111), Pt grows in a layer-by-layer growth mode, but if the gold substrate is exposed to an acidic environment prior to Pt deposition, then the substrate becomes nanoscopically rough (islanded) and Pt growth follows a pseudo-Stranski–Krastanov (SK) growth mode in which an initially thin wetting layer becomes rougher with increasing film thickness. An analysis of curvature effects on epitaxial growth mode shows that thermodynamic curvature effects involving surface stress are negligible for the Pt/Au(111) system. Rather, the apparent SK growth is linked to kinetic effects associated with inhomogeneous in-plane elastic relaxation of Pt films on rough surfaces that drive Pt atoms from pits to the tops of islands in the early stages of growth. They observe that mean island height initially increases and subsequently decreases in early growth (i.e., up to 4 nm film thickness) and mean island spacing remains initially constant and subsequently increases (beyond 2 nm film thickness).

The evolution of the interface width has been analyzed experimentally and numerically by Qi et al. [21, 26] in their work on film growth on non-planar substrates. Interestingly they report on the growth of ZrO$_2$ films deposited on to BK7 glass substrates of roughness 0.4 nm by ion beam sputter deposition. The films were deposited for durations ranging from 10 to 150 min at a deposition rate of 1 nm/min which is the upper limit of rates of deposition used in the current study. The authors show that the early stages of growth can be characterized by three main quantities; (1) the height-height correlation function determined as a function of lateral position, $r$ and deposition time, $t$ (2) The interface width, $w$ which is a measure of the interfacial roughness and (3) lateral correlation length, $\xi$ which is defined as the largest distance in which the height of particles is still correlated. They find that the interface width goes through a minimum and the lateral correlation length goes through a maximum in the initial stages of growth, i.e for low deposition times.
Galdikas [20] has done detailed modeling of early stages of thin film formation on rough substrate surfaces using a phenomenological model. The author has introduced surface potential dependent sticking coefficients to allow for substrate roughness. The kinetics of the three main characteristics: surface coverage, island density and average island size are analyzed. From the theoretical investigation it is found that the shape of the kinetic curves qualitatively differ for 2D and 3D island growth mode. The island density at any instant of time is given by the expression

$$\frac{dn}{dt} = \frac{1}{2} \alpha_{AA} t_0 (\varphi_s + a(t) \varphi_s^*) + \alpha_{col} C_{col} \left(1 - \varphi_C - \varphi_B\right)$$

(3.16)

The calculated dependence of the total amount of deposited material on deposition time was normalized to the number of fully covered monolayer (equivalent thickness) for different ratios of parameters $\alpha_{AA}$, $\alpha_{AC}$ and $\alpha_{AT}$, i.e. for different film growth mechanisms. The surface coverage by islands increases when (1) the arriving atom sticks at the already existing single adatom with probability (or sticking coefficient) $\alpha_{AA}$ and or (2) it sticks at the edge of already existing island with probability $\alpha_{AC}$. Surface coverage, initially is therefore completely dependent on sticking coefficients which are in turn dependent on substrate roughness.

The other parameters of relevance to the current work are the island size and density. The process of island migration was described by a parameter $\beta$, which is defined as the radius of circle within which the mass center of island mass can move. At higher values of $\beta$ the coalescence (mobility coalescence) occurs at lower values of surface coverage. The island density also depends strongly on the parameter $\lambda$, which represents the diffusion length of adatoms. With increase in the parameter $\lambda$, the number of islands decreases and the size of islands increases, because more adatoms can reach and stick at the existing islands.

The author has made a very detailed analysis of the kinetics of island size and densities, but only relevant portions are discussed here. The calculated kinetics of island densities revealed that, for fixed value of $\beta$, the island density is constant over a large range of deposition times and decreases drastically thereafter. In contrast for small value of $\lambda$, there is a very sharp initial increase in the island density followed by an exponential decrease beyond a critical deposition time. Similar analysis of the dependence of island size on $\beta$ for fixed $\lambda$ values shows that for low $\beta$ values there is an initial increase in
island density beyond which it remains constant. The island density then decreases only for very long durations of deposition (in this case > 1200 s). As the $\beta$ values increases the duration for which the island density remains constant decreases presumably due to increased surface diffusivity.

The temperature dependence of $\beta$ has been expressed in the following equation

$$\beta(t) = \beta_0 \exp \left(-\frac{Z(t)}{Z_{\text{max}}}\right)$$  \hspace{1cm} (3.17)

where $\beta_0$ is the pre-exponential factor, $Z(t)$ is the ratio of the surface coverage $\varphi_c(t)$ with islands at a time $t$ to the relative number of islands $n(t)$ on the surface at the same time $t$. $Z_{\text{max}}$ is the maximum island size at which it becomes immobile, or two islands touch each other. It can be shown from this equation that for small values of $t$ there will be an initial decrease in diameter of the clusters before it reaches a critical size beyond which it will increase. This is due to the decrease in island density at longer durations of deposition.

The phenomenological models developed by Galdikas [20] and Qi et al. [21], thus shows that films deposited on rough surfaces exhibit very different kinetics of surface coverage, diffusion and island migration than films deposited on flat substrates. There are two competing processes at the early stages of film growth; desorption and diffusion. A substrate with high roughness can be modeled as having a number of peaks and valleys, like a sinusoidal wave. At peak positions, initially, desorption dominates over the diffusion process leading to either an increase in island density or constant island density up to a critical duration of deposition beyond which the normal dynamic scaling behavior occurs. Hence the films remain discontinuous for larger effective thickness retaining the “memory” of the substrates for larger thickness. The growth on rough substrates can thus be divided into two broad regimes abnormal and normal coalescence. The abnormal coalescence observed in the Ag and Au films deposited on CCG substrates, in the present work, can be explained within the framework of the phenomenological models developed by Galdikas and Qi et al. [20,21,26]. Evidently, surface coverage is limited by roughness of the substrates which decreases the sticking coefficients. These and other earlier reports of film deposition on rough substrates have focused solely on smoothening of films grown on such substrates and decreasing the island density to form continuous films. In
the present work it is demonstrated that substrate roughness can also be used to control shape and size of nanoclusters in the early stages of thin film growth making it a viable technique for the fabrication of nanostructured thin films.

3.6. Summary

In summary, the growth process of metal thin films (Ag and Au) by ion beam sputter deposition (IBSD) technique is studied. It is found that the IBSD offers very fine control over growth of the films compared to DC sputtering and thermal evaporation technique. It is observed that IBSD offers a great degree of control over the size, shape and interparticle spacing in the nanostructures and nanostructured films. The films growth is discontinuous at low ion energy deposition and become island like and continuous with the increase of deposition time or rate of deposition. This process of growth is very well explained by the theory of growth and nucleation.

A variety of nanostructures such as non-regular array of nanoparticles, nanoneedles and nanoclusters have been realized. Discontinuous Ag and Au thin films were grown on different substrate by IBSD. Two distinct regimes of coalescence are observed depending on the substrate roughness. Normal coalescence, defined as the regime where grain coarsening as a function of increasing deposition duration and temperature occurs, is observed on smooth BSG substrates. Abnormal coalescence defined as the regime where the cluster sizes decrease as a function of increasing deposition duration and temperature occurs, is observed on rough CCG substrates.
References