The patterns arising from the interplay of colloidal gold nanoparticle solutions containing polyvinyl alcohol spin coated on different substrates have been investigated. High Resolution Transmission Electron Microscope results show chain-like assemblies and direct attachment of spherical shape gold nanoparticles with different size in the polyvinyl alcohol matrix. X-Ray photoelectron spectroscopy analysis of the C 1s peak shows three different Au-polyvinyl alcohol bands (-CH₂, -OH and C=O) which accounts for the effect of the Au particle size in the gold-PVA films. Dewetting of Indium Tin Oxide substrates by 6 nm Au nanoparticles/polyvinyl alcohol colloidal solution induces concentration dependent cellular structures and fingering instability patterns which were duly reproduced using Monte Carlo simulations. Our results ascertain the importance of nanoparticle size, substrate type, orientation and surface roughness on the pattern formation. In addition, we demonstrate that pattern formation on different substrates takes two different routes based on nanoparticle mobility rate, evaporation chemical potential and nanoparticle density.
6.1. Introduction

Noble metal nanoparticles (NPs) have received a great attention in recent years due to their profound applications in various fields of science. Inherent properties of these particles depend on their size, shape, composition and crystallinity [1]. Their assembly into well defined structures has been widely investigated after spin coating of their colloidal solutions on planar substrates. These solutions wet the substrates and start to evaporate and eventually form films which show patterns of different shapes and sizes. Factors like nanoparticle diffusion, concentration, evaporation conditions, film thickness, frictional forces, chemical potential, temperature as well as liquid-liquid, nanoparticle–nanoparticle, nanoparticle–liquid, nanoparticle–substrate and liquid–substrate interactions have been reported to play a major role in the formation of the self-assembly of these patterns [2-5].

Recently the effort has been extended beyond the assembly of metallic nanoparticles alone to include nanoparticles and polymers. These efforts were driven by the need to improve the film stability, development of 2D and 3D structures and to capitalize on the induced new electronic properties attributed to the interaction between metallic nanoparticles and polymers. For example, it is well known that coupling of metallic plasmon resonance with molecules causes enhancement in the linear and nonlinear optical properties such as Surface-Enhanced Raman Scattering (SERS) signals. Polavarapu et al. reported the induced assembly of gold nanoparticles in water soluble conjugated polymers [6]. They showed a simple way to assemble the citrate reduced gold (Au) nanoparticles into nanochains where a longitudinal plasmon resonance band is formed and tuned from visible to near infrared by adjusting the polymer/Au molar ratio. Huang et al.
reported the electrochemical synthesis of gold nanocrystals and their 1 & 2D assembly using poly (N-vinylpyrrolidone (PVP) [7]. Mueggenburg et al. presented the 2D nanoparticle superlattices using dodecanethiol-ligated gold nanocrystals suspended in toluene spread across the top of a water droplet placed on a silicon nitride substrate [8].

To capitalize on the properties of PVA such as thermal stability, chemical resistance and of metal nanoparticles, we investigate on the pattern formation resulted from the self assembly of gold nanoparticles in PVA mix spin coated on different substrates. A modified pseudo-2D lattice gas-based Monte Carlo simulation is used to understand the Au-PVA film dewetting mechanisms and to reproduce the patterns that were observed experimentally. We demonstrate that the type of pattern formed is strongly dependent on many parameters such as Au particle size, type, orientation and roughness of the substrate and PVA concentration.

6.2. Experimental

Au NPs colloids of 1.6% wt concentration purchased from Nanopartz USA with < 0.1% carboxylic acid functionalized hydrocarbon capping agent and < 0.1% hydroxide in distilled water were used for the self-assembly investigations. The particle diameter ranges from 6 nm to 100 nm with peak surface plasma resonance (SPR) ranging from 512-590 nm in colloids of pH 6-8, Zeta potential of -20 mV and conductivity of 0.0275 mS/cm. PVA dissolved in deionized water at different concentrations were mixed with Au NPs colloids at room temperature and spin coated at 8000 rpm for 30 seconds on ITO, smooth and rough GaAs(100), Si(100), Si(111) and Highly Oriented Pyrolytic Graphite (HOPG) substrates. All Si(100) and
Si(111) substrates were cleaned with acetone, ethanol and dried before Au-PVA film spin coating.

To investigate the effect of surface roughness on the pattern formation, GaAs(100) substrates were etched using a mixture of sulfuric acid (H\textsubscript{2}SO\textsubscript{4}), hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}) and water. After etching the substrates were immediately loaded into ultra-vacuum preparation chamber of X-ray Photoelectron Spectroscopy (XPS) system and degassed for 48 hours at temperature of 200 °C. After degassing the substrates were annealed at 600 °C for 30 minutes and the temperature was measured using an optical pyrometer with an accuracy of ± 25 °C. Each GaAs substrate was investigated along (110) direction to allow surface structure observations by Reflection High Energy Electron Diffraction (RHEED). In addition, Au NPs-PVA samples were characterized by High Resolution Field Emission Transmission Electron Microscope (HR-FETEM) (JEM-2100F) operated at 200 kV and Veeco multi-mode Atomic Force Microscope (AFM) operated in tapping mode using high resolution tips of radius< 1 nm. For the Scanning Tunneling microscope (STM) measurements, both constant-current and constant-height modes were used while scanning the ITO samples in air using conducting Platinum Iridium (PtIr) tips of diameter less than 0.048 mm. Typical sample bias voltages used were 3– 4 V.

Surface composition of the dewetted films and interaction information between Au NPs and PVA were deduced from the XPS analysis data obtained by an Omicron Nanotechnology XPS system working with a monochromatic Al K\textalpha radiation (hv = 1486.6 eV) of source voltage 15 kV and emission current of 20 mA. The UV absorption spectra were collected using HP/Agilent 8453 UV-Vis Spectrophotometer.
The self-assembly process of gold nanoparticles was simulated by the Monte Carlo program [4, 9, 10] based on coarse-grained lattice gas model and the energy of the system is determined by the Hamiltonian:

\[ H = -\varepsilon_n \sum_{\langle ij \rangle} n_i n_j - \varepsilon_i \sum_{\langle ij \rangle} l_i l_j - \varepsilon_m \sum_{\langle ij \rangle} n_i l_j - \mu \sum_{i} l_i \]  \hspace{1cm} (6.1)

where \( \varepsilon_n, \varepsilon_i, \varepsilon_m \) are the interaction energies for adjacent sites \((i, j)\) filled by nanoparticles, liquid, and nanoparticles-liquid respectively. The sum \( \sum_{\langle ij \rangle} \) includes the nearest neighbors and the next-nearest neighbours which are given weightings of 1 and \( 1/\sqrt{2} \) respectively. The symbol \( \mu \) is the solvent chemical potential that represents the free energy difference between the liquid and vapor phase. It controls the evaporation and condensation of the liquid.

**6.3. Results and discussion**

Figure 6.1 shows the general morphology of the Au NPs in PVA matrix imaged on TEM copper grid. Typical spheroids shape NPs can be seen with the particle size distribution shown in the inset of Figure 6.1(a).
Figure 6.1: (a) HRTEM showing gold nanoparticles and their size distribution (inset) in PVA matrix, (b) SAED diffraction pattern showing expected lattice reflections of gold particles, (c) HRTEM revealing (200) lattice spacing.

As a result of Au NPs-PVA interaction, chain-like assemblies (enclosed by a circle) and direct attachment of small to large (enclosed by a square) Au NPs can be observed. The chain assembly might be originated due to the carboxylic acid functionalized hydrocarbon capping agent used during the sample preparation. These assemblies are characterized by a bimodal particle...
size distribution with peak size at 6 nm and 10 nm. Furthermore, the particles show the polycrystalline nature of fcc-Au with two distinct lattice reflections (111) and (200) at respective interplanar spacings $d_{hkl}$ of 0.2306 nm and 0.2001 nm as revealed by selected-area electron diffraction (SAED) in Figure 6.1 (b) and HRTEM in Figure 6.1 (c). All other samples with particle size from 10-100 nm show similar spheroids morphology and fcc structure.

The UV absorption spectra of the Au NP solutions with and without 0.2% PVA display strong peak which is Au particle size dependent ranging from 517 nm to 524 nm for particles size of 6 nm to 30 nm. This peak-Au particle size dependence is well known characteristic of plasmon resonance bands of the gold nanoparticles [11]. Figure 6.2 shows the UV spectra for 1.5 ml of 6 nm and 30 nm Au NPs after water and 0.2% PVA dilution at different volumes. It is clear from Figure 6.2 (a) and 6.2(c) that diluting the 6 nm and 30 nm Au NP solutions by water does not have any effect on the absorbance of Au NPs. On the contrary, upon addition of 0.2% PVA at different volumes, the intensity of the bands at 517 nm and 524 nm for the 6 nm and 30 nm Au NPs decreases compared to that of water for the PVA volumes of 0.3 ml to 1.2 ml as found in Figures 6.2(b) and 6.2(d) respectively. In addition, broadening in the UV spectra is observed after the addition of PVA which suggests agglomeration of Au NPs or reduction in the distance between Au NPs to take place. Therefore, justifying the slight red shift in the UV spectra observed after the addition of PVA particular for the 30 nm Au NPs. It should be noted that PVA alone will not absorb the light in the visible range. However, PVA is expected to affect the Au NPs dispersion [12], Au NPs shape [13] and change the dielectric constant of the Au NPs surrounding media- all of these can lead to the observed changes in the UV intensity and to the shift of Au NPs plasmonic peak. Trends similar to those
seen in Figures 6.2 (b) and 6.2(d) have been reported by Vodnik et al. [14] and attributed to the interaction between Au NPs and PVA.

![Figure 6.2: UV absorption spectra of Au NPs upon addition of different amounts of water and 0.2% PVA solutions. (a) 1.5 ml of 6 nm Au NPs diluted by 0.3 ml to 1.8 ml water, (b) 1.5 ml of 6 nm Au NPs diluted by 0.9 ml to 1.8 ml PVA solutions, (c) 1.5 ml of 30 nm Au NPs diluted by 0.3 ml to 1.5 ml water, (d) 1.5 ml of 30 nm Au NPs diluted by 0.3 ml to 1.8 ml PVA solutions.]

6.3.1 XPS analysis of Au NPs size effect in Au-PVA films

In order to explore the interaction between Au nanoparticles and PVA polymer, XPS was employed. The XPS data shown in Figure 6.3(a) describes a deconvolution of C 1s spectrum for pure PVA with three carbon components -CH₂, C-OH and C=O at binding energies of 283.8, 285.3 and 287.9 eV respectively. Upon mixing 0.2 wt% of PVA with 6 nm Au
nanoparticles, a Au-PVA film is formed. The film exhibits remarkable decrease in the C=O peak intensity together with chemical shift of 0.3 eV and increase in the C-OH signal as depicted from Figure 6.3(b). It may be noted that, when the Au particle size is increased to 30 nm and 100 nm (Figure 6.3(c)), increase in C-OH bonds formation and reduction in C=O bonds is observed respectively. The chemical shift to higher binding energies of the C-OH peaks in the films contain Au nanoparticles compared to that of pure PVA implies that C-OH moieties act as links between Au nanoparticles and PVA molecules. This is possible if the interaction between Au NPs and PVA molecules takes place where the C and Au atoms act as electrons acceptors and donors respectively. It is very interesting to see that 30 nm and 100 nm Au particles are more effective in cross-linking to the PVA molecules compared to that of 6 nm. This observation contradicts the fact that small Au NPs should be more effective in cross-linking as they share a large number of surface atoms with PVA molecules and suggests Au particle size dependent linkage mechanism. In fact this is apparent from the decrease of -CH$_2$ component (peak areas labeled by 1 in Figures 6.3(a) and 6.3(b)) which indicates that the PVA molecules on the surface might be broken into much smaller molecules upon mixing with larger Au nanoparticles. This explanation is supported by AFM results shown in Figures 6.7(a)-6.7(f).
6.3.2 Effect of substrate type, PVA concentration and Au particle size on pattern formation

Figure 6.4 shows the effect of substrate on the pattern formation of 0.2 wt% of PVA with 6 nm Au nanoparticles spin coated on Si(100), Si(111), ITO, and HOPG. Although there have been numerous studies of dewetting of uniform polymers and nanoparticles films [15,16] studies of the effect of substrate type are limited. Previous studies [17,18] on evaporation of nano-
colloidal indicate the formation of holes in the dewetting films similar to those observed in Figure 6.4(a) on Si(100). The holes can be described as nonequilibrium patterns which split into branches as they grow in size. We found that the rate of holes coalescence and splitting into branches is substrate type and orientation dependent and it is faster on ITO compared to that observed on Si (100) and Si (111) substrates as shown in Figures 6.4(a) and 6.4(b) respectively.

Figure 6.4: AFM images of 0.2 wt% of PVA with 6 nm Au nanoparticles spin coated on different substrates: (a) Si(100), (b) Si(111), (c) ITO, (d) HOPG.

The topographic image shown in Figure 6.4(d) and its corresponding phase image shown in Figure 6.5(a) suggest that PVA cause agglomeration of Au
NPs on HOPG substrates where Au NPs are found to be surrounded by PVA chains with Au NPs-PVA decorated tails.

Figure 6.5: (a) AFM phase image of 0.2 wt% of PVA with 6 nm Au nanoparticles spin coated on HOPG. Inset shows Au NPs agglomeration and surrounded by PVA chains with PVA Au decorated tails, (b) STM height image showing ITO substrate with roughness of 0.9 nm.

Although the branches formation was found to be faster when Au NPs-PVA is deposited on ITO compared to the other substrates, it turns out to be also PVA concentration and Au NPs size dependent. Experimental realization of concentration and size effects are revealed in Figure 6.6 and Figure 6.7 respectively. At 0.2 and 0.1 wt% PVA concentrations, both cellular like and
branch structures are observed as depicted in Figures 6.6(a) and 6.6(b). The reduction in the PVA concentration to 0.05 wt% causes the branch structures to dominate as seen from the AFM height image shown in Figure 6.6(c) and its corresponding AFM phase images shown in Figure 6.6(d). Careful investigations revealed that, Au NPs selectively decorate the PVA branches (appearing in brown in the AFM image shown in Figure 6.6(d)).

Figure 6.6: AFM images showing pattern formation after deposition of Au 6 nm in PVA mix at different PVA concentrations on ITO substrates, (a) 0.2 wt%, (b) 0.1 wt% and (c) 0.05 wt% (d) phase image corresponding to the data shown in (c).

The results presented above clearly indicate the distinction in the degree of branching between Si(100), Si(111), HOPG and ITO substrates. The latter has high degree of branching due to the effect of surface roughness produced
during the ITO sample preparation. Indeed, this preparation induced roughness of 0.9 nm can be seen from the STM image shown in Figure 6.5(b). The effect of roughness stems from the fact that it increases the rate of coalescence of the holes during the dewetting process which leads to the branch enhancement.

Figure 6.7: AFM high images of 0.2 wt% of PVA spin coated on ITO substrate with different Au nanoparticles size; (a) 6 nm, (b) 30 nm, (c) 40 nm, (d) 70 nm, (e) 80 nm and (f) 100 nm. Inset of (f) is the zoom of area enclosed by square in (f) showing disintegration of PVA molecules.
It is expected that as the roughness is increased complete breaking or disappearance of branching to take place. An example of this case will be presented later from the thermal induced roughness of 1.8 nm of GaAs substrate. The results presented in Figure 6.7 demonstrate the effect of increasing the Au nanoparticle size from 6 nm to 100 nm on the pattern formation. As it can be seen at high particle size the cellular and branching structures disappear - a sign of bending or bond breaking of PVA molecules. Although the AFM and the XPS results show the effect of the Au particle size in the Au-PVA films, we have no explanation on the mechanism behind the disintegration of PVA and is subject for further investigations.

In an attempt to understand the development mechanism of the observed structures, we have carried out computer simulations by varying parameters such as nanoparticle mobility rate, evaporation chemical potential and nanoparticle density. The results suggest that most of the experimentally observed structures take two different routes in their development attributed to the well known spinodal dewetting [19] or fingering instability mechanisms [20].
Figure 6.8 (a)-(l) show simulation replication of the holes and cellular structures as solvent evaporation takes place on a \(1024 \times 1024\) lattice with low temperature \(k_B T/\varepsilon = 0.5\), high chemical potential \(\mu/\varepsilon = -2.4\), moderate particle coverage and low nanoparticles mobility ratio = 25. Dark and bright areas represent the substrate and nanoparticles film respectively.

Indeed computer simulation results shown in Figures 6.8(a)-(l) show the formation of holes and cellular structures in the films which replicate the patterns obtained after AuNPs-PVA deposition on ITO substrates at PVA concentrations of 0.2 wt% and 0.05 wt%. Initially, few randomly positioned holes are formed via infrequent thermal nucleation of the metastable solvent
film [Figure 6.8(b)]. As the solvent evaporation increases, the holes grow and reach the dual-scale structure stage [Figure 6.8(d)]. The transition to cellular network, characteristic of spinodal dewetting mechanism then takes place [Figures 6.8(h)-(l)]. Driven by Au particle size at late stage of the dewetting of the ITO substrates, the cellular structures can become unstable and split leading to the formation of branches which can further breakdown into short branches or isolated units as shown in Figure 6.7.

It is well known that thin liquid films can become structurally unstable and dewet, forming holes [Figures 6.9(a)-6.9(e)] which subsequently coalesce, grow in size and fluctuate leading to local variations in the curvature of their rims [Figures 6.9(f)-6.9(g)]. These variations in the curvature establish Laplace pressure gradient which forces nano materials to move from thicker regions to thinner regions to suppress the fluctuations. As the thinner regions in the rims provide less resistance to the capillary flowing driving forces, particles will move faster compared to that of the thicker regions, hence result in the development of fingering patterns as seen in Figures 6.9(h)-6.9(l). This fingering instability mechanism is the proposed second route of the development of the experimentally observed structures formed on Si(100) and Si(111) shown in Figures 6.4(a) and 6.4(b) respectively. A strong tendency of holes coelence and a high degree of fingering can cause thin ribbons development between neighboring holes [Figure 6.9(l)] and consequently their disintegration into high density branched structures [21]. This branching mechanism stems for the dense branching observed after AuNPs with 0.05wt% PVA film spin coated on ITO respectively.
Figure 6.9(a)-(l) show simulation replication of the holes and fingering structures as solvent evaporation takes place on a $1024 \times 1024$ lattice with low temperature $k_{B}T/\varepsilon = 0.2$, high chemical potential $\mu/\varepsilon = -2.8$, moderate particle coverage and low nanoparticles mobility ratio = 30. Dark and bright areas represent the substrate and nanoparticles film respectively.

6.3.3 Surface roughness effects on pattern formation

Having discussed the effects of substrate type, PVA concentration and Au particle size on pattern formation, we turn our discussion on the effects of surface roughness. Earlier in section 6.3.2 the enhancement in the branching on the ITO was attributed to the surface roughness compared to other substrates. Here we further give experimental evidence obtained by using smooth and rough GaAs (100) substrates. Figure 6.10 (a) shows the RHEED
pattern with sharp spots indicative of rough surface caused by desorption of As atoms after annealing the GaAs substrate at 600 °C. The thermal induced roughness is supported by the AFM results shown in Figure 6.10 (b). High resolution AFM image shown in the inset of Figure 6.10(b) reveals surface decomposition into oval-like plates surrounded by depressions seen in the dark contrast. The surface is densely covered with irregular structures with RMS roughness of 1.8 nm.

Figure 6.10: (a) RHEED pattern of the decomposed GaAs(100) surface. (b) AFM height image showing rough after GaAs thermal surface decomposition, inset shows high resolution AFM image indicating oval-like plates formed after GaAs thermal surface decomposition. (c) and (d) show the effect of substrate on the pattern formation of 0.2 wt% of PVA with 6 nm Au nanoparticles spin coated on rough GaAs and smooth GaAs respectively.
Spin coating of 0.2 wt% of PVA with 6 nm colloidal Au nanoparticles on this substrate, results in very fast evaporation of the dewetting film and formation of the Au nanoparticle clusters connected by PVA network [seen in bright color in Figure 6.10(c)]. This case is completely different from the pattern formation on smooth GaAs(100) substrate seen in Figure 6.10(d) where the dewetting film is ruptured to form holes of equal size similar to that found on Si(100) and those replicated by simulation seen in Figure 6.4(a) and Figure 6.8(d) respectively.

Although, the Hamiltonian used in our simulation model did not consider the solvent-substrate and nanoparticle-substrate interaction. Simulation results reported did provide general evidence and support the experimental results on pattern formation regardless the substrate type. Therefore, one would expect if the solvent-substrate and nanoparticle-substrate interaction were considered only the strength and the rate by which the patterns are formed will be different and the type of the patterns will stay the same- as those seen experimentally and supported by simulation results shown in Figures 6.8 and 6.9.

6.4. Conclusions

Self-assembly of Au nanoparticles/ PVA mixtures have been studied using TEM, XPS and AFM techniques. When these mixtures are spin coated on different substrates they show different patterns ranging from holes to branching patterns which were duly reproduced using Monte Carlo simulations based on Ising lattice gas model. These results suggest that most of the experimentally observed patterns take different routes in their development attributed to the spinodal dewetting or fingering instability mechanisms. Furthermore, reduction of PVA concentration in the mixture resulted in the development of both cellular and branch
structures, while increasing Au particle size in PVA mixture leads to the disintegration of PVA molecules on ITO substrates. This size effect accounts for the observed variation in the PVA bands (CH$_2$, C-OH and C=O) in the Au-PVA films analyzed by XPS. In addition, surface roughness was found to have an impact on the rate of evaporation of the dewetted layer containing the mixture and induces Au clustering.
References


