Chapter 6

Effect of Annealing on Spherical Shaped Silver Nanoparticles

Metal nanoparticles give typical absorption spectra due to surface plasmon resonance (SPR) arising from oscillation of conduction electrons which depends upon the shape and size of the particles. To obtain various size and shape of nanoparticles, there are numerous ways viz. changing the concentration of the starting materials in chemical reduction [1], changing matrix, changing temperature of synthesis, photoreduction method [2-3], postsynthesis annealing, etc. Annealing is well known to bring more order in the system by changing particle size, orientation, alignment etc. to give lesser entropy state. After annealing the morphology of the nanoparticles changes and a shift of SPR peak occurs [4, 5]. The size of the particles and their number change as the annealing time of the film increased, yielding a plasmon absorption band whose intensity is correlated to the silver nanoparticles density [6]. Annealing process also affects in the floating silver nanoparticles which are applied in Organic Non Volatile Memory transistors [7]. In this Chapter, we report the effect of annealing on the surface morphology and optical properties of spherical shaped silver nanoparticles synthesized by chemical reduction method. We observed that with the increase in annealing temperature, size of the particle increases and shape of the particle also changes. Also blue shift of surface plasmon resonance peak occurs with the increase in annealing temperature.

6.1 Experimental

Spherical shaped nanoparticles are prepared by chemical reduction method as reported in Chapters 2 and 3. The composite films containing spherical silver nanoparticles are then annealed at five different temperatures (373K, 423K, 473K, 523K and 573 K) in vacuum for 2 hrs. Characterization of the annealed films are done by the usual methods, SEM, XRD, UV-Visible absorption, and photoluminescence (PL) spectra.

6.2 Results and Discussion

6.2.1 Morphology

The film morphology and particle size distribution of Ag-PVA nanocomposite is studied by SEM. The obtained SEM images are shown in figure 6.1(a-f). As is expected with annealing process, average size of the particles is seen to increase with the increase in annealing temperature. Also, in two of the cases (annealing temperatures 523 and 573 K), we observed formation of nanocubes and nanorods respectively. The average size of the nanocubes is in the range of 200-400 nm. The length of the nanorods is in micrometer range whereas the diameter is in nm range. It is to be mentioned that the unannealed film show predominance of spherical nanoparticle of average particle diameter of 20 nm [8, Chapter 3].

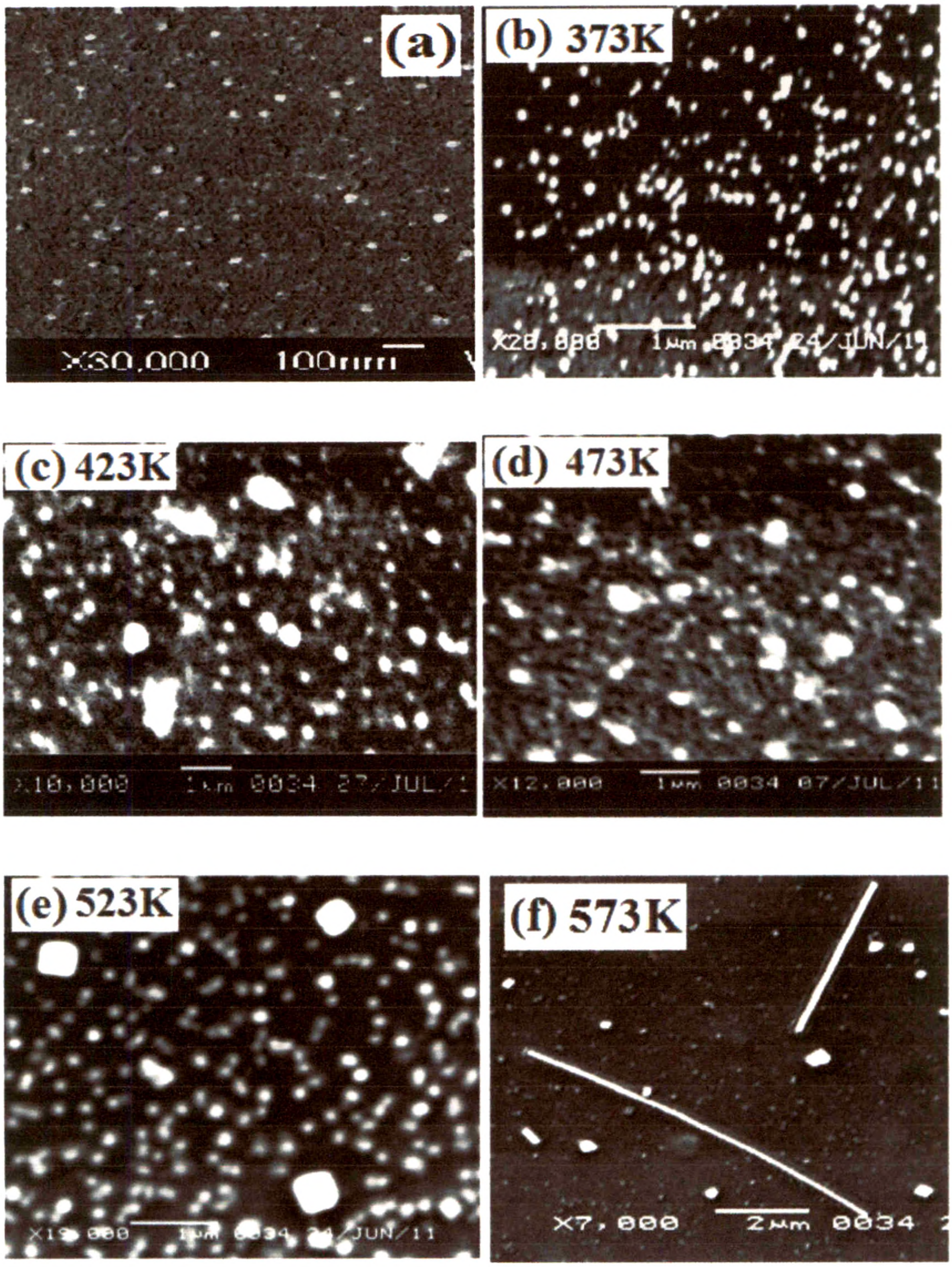


Figure 6.1: SEM images of the samples (a) before annealing and after annealing at different temperatures (b) 373 K (c) 423 K (d) 473 K (e) 523 K (f) 573 K

6.2.2 Structural properties

In figure 6.2 we have shown the XRD spectra of the annealed films along with the unannealed one. The XRD patterns of the nano composite films show a strong characteristic peak of silver nano around $2\theta = 38^0$ for (111) crystalline plane [9] for all the films for five different annealing temperatures.

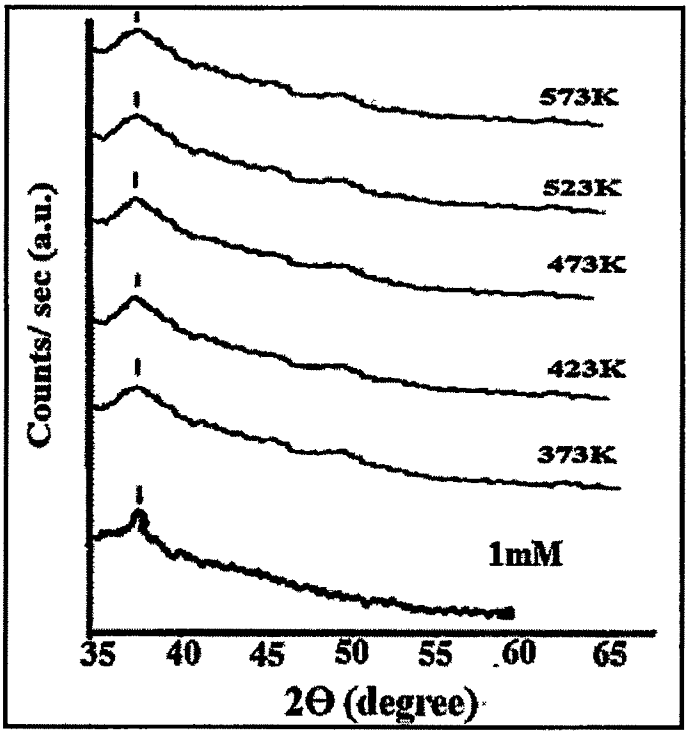


Figure 6.2: XRD images of the samples after annealing at five annealing temperatures

6.2.3 Optical properties

In figure 6.3, we show the UV-Visible absorption spectra for these five films along with the unannealed one. This shows strong plasmon resonance peak which is a clear consequence of formation of nanosized particles [10]. The size and the shape of the particles have a great impact on the UV- Visible absorption spectra. With the increase in annealing temperature, the surface plasmon peak position is blue shifted. Also we observe that beyond annealing temperature of 373K, the peak position is shifted to 411 nm, a blue shift of 30 nm with respect to the unannealed one [8]. For the two films which are annealed at 523 K and 573 K, the shape of the particle changes to cubic and rod respectively and the corresponding absorption peak positions are observed at 329 nm and 320 nm. Also, we can see small hump which are possibly due to the mixing of spherical shaped nanoparticles of different sizes along with the cubes and rods. The curve broadens more towards red region indicating distribution of particle sizes of little wide range and the absorption peak corresponds to the value for average particle size. The shape of the SPPR spectrum is determined by the relative dimensions of the particle to that of the wavelength of incident electromagnetic (EM) radiation. For nanoparticles much smaller than the wavelength of light, the EM field is uniform across a particle such that all the conduction electrons move in-phase producing only dipole-type oscillations manifested by a single, narrow peak in the SPPR spectrum. As the size increases, the field across the particle becomes nonuniform, and this phase retardation broadens the dipole resonance and excites higher multipole resonances, such as the quadrupole, octupole, etc. leading to several peaks in the spectra. [11]

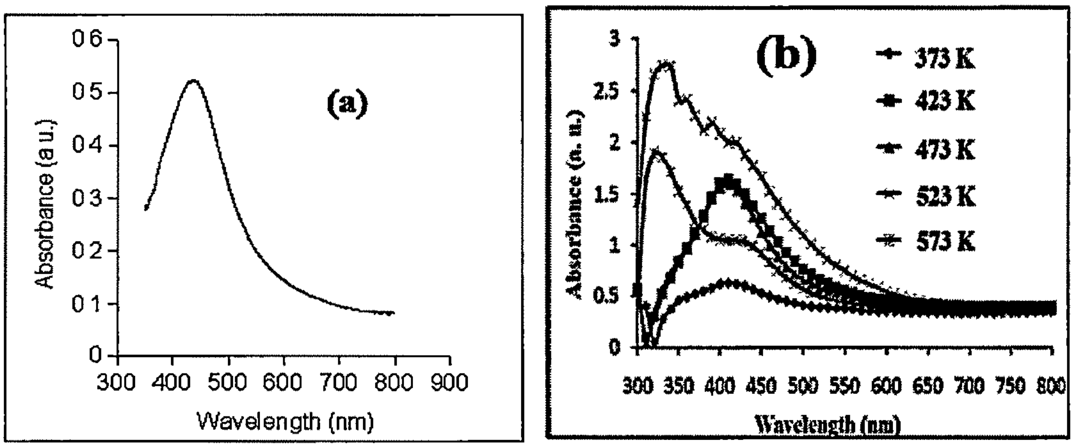
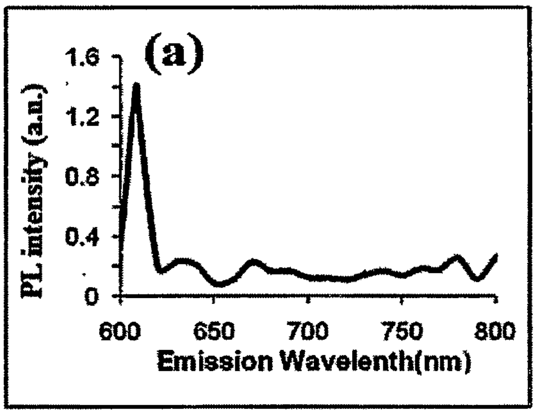


Figure 6.3: Surface Plasmon Resonance spectra of the samples (a) before annealing and (b) after annealing at different temperatures

In figure 6.4, we show the room temperature photoluminescence (PL) of these annealed films for excitation wavelength of 350 nm. These show emission band nearly at 450 nm. With the increase in annealing temperature, the PL peak is seen to have red shift. The fact that the PL peaks are solely due to the presence of silver nanoparticles has been confirmed by absence of PL peak in the pure PVA film. This result is similar to what obtained by Henglein et al. [12] for Ag nanoparticles reduced in the presence of polymers and Zheng et al. [28] for dendrimer-encapsulated silver nanodots. For the unannealed sample, the emission peak is obtained at 608 nm for excitation wavelength of 405 nm [13] but no PL peak for excitation wavelength of 350 nm.



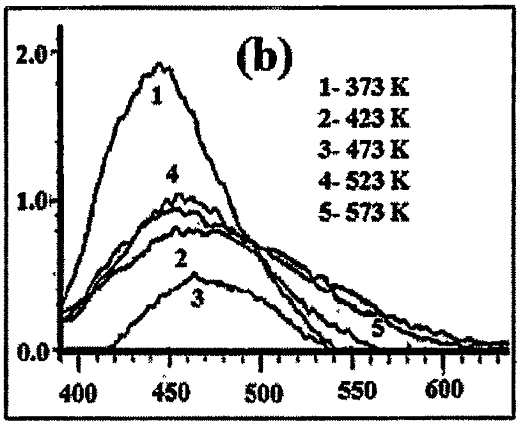


Figure 6.4: Photoluminescence spectra of the samples (a) before and (b) after annealing at different temperatures

6.3 Summary

The composite films with spherical shaped silver nanoparticles are annealed in vacuum to investigate its effects on morphology, structural and optical properties. A clear blue shift in surface plasmon resonance peak is observed with increase of annealing temperature. The observed blueshift correlates well with the geometrical and dimensional changes of silver nanoparticles as revealed by SEM analysis. There is remarkable change in size and shape of nanoparticles on annealing. In one case we observed nanorod formation by aligned assembly of nano particles. This study offers an interesting approach to alter surface plasmon resonance characteristics and thus optical transmission properties of metal nanoparticles. Also the excitation wavelength of PL emission is seen to decrease gradually as the size of the particles increases and also as shape changed from sphere to cube to rod.

Table 6.1: Summary of results of Chapter 6

Sl. No.	Anne-aling Durat-ion	Anneal-ing Tempe-rature	SEM		XRD Studies	UV-Visible peak position (nm)	PL peak Position (nm)
			Size (nm)	Shape			
1	2 hrs.	373K	100	spherical	$2\theta=38^0$ for (111) plane.	411	Emission band~450 nm Excitation Wavelength 350 nm
2		423 K	300-400	spherical		410	
3		473 K	400-500	spherical		408	
4		523 K	300-400	cubic		329	
5		573 K	Nanorod length-µm Diameter-nm	Spherical and rod		320	

6.4 References

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