Effect of reduction through the Spin Coating growing Silver thin Films Nanostructure

Ari A. Yatem[1]*

[1]*Department of Physics, Faculty of Science, University of Zakho, Zakho, Kurdistan Region, Iraq*

ABSTRACT

Silver (Ag) thin-film nanostructures are prepared on the glass surface through a dependable method called spin coating. Silver nitrate ($AgNO_3$) has been utilized as precursors, proceeded by the thermal reduction in the H_2 atmosphere, and some of the chemical reductions such as sodium borohydride ($NaBH_4$) solution, and hydrazine hydrate solution (N_2H_4). The effects of several reductants have been discussed. The structure, morphology, and absorbance spectra of the deposited silver thin films have been characterized and measured by using the following techniques X-ray diffraction (XRD), Scanning electron microscope (SEM), as well as UV-visible- NIR absorption spectroscopy, to study more about how the reduction procedure affects the formation of silver nanoparticles. As a result, thermal reduction in the H_2 atmosphere is more effective than the chemical reduction in aqueous sodium borohydride and hydrazine hydrate solution for growing consistently sized dispersed silver nanoparticles.

Keywords: Ag thin film nanostructures, Reducing agents, Spin Coating, Localized Surface Plasmon Resonance (LSPR), Reduction.

1. Introduction

Nanoparticles have gained a lot of attention in the scientific community due to their massive surface area to volume ratio and strong reactivity with unrivaled features. Nanoparticles can act as a strong link between bulk materials and molecular or atomic structures[1]. A bulk material's physical qualities remain constant regardless to their form and size, However, at the nanoscale, the morphological substructure of the material, the size, and structures are the primary determinants of its physical features. Because materials function differently at the nanoscale, they emerge with a few new characteristics, such as some materials becoming explosive, changing their melting point, or revealing a new attribute[2]. Silver nanoparticles (Ag-NPs) have unique and size-related physical and chemical characteristics that set them apart from their bulk materials[3]. Ag-Nps have unique physical, optical and chemical properties that make them useful in a variety of sectors, including renewable energies, catalysis, photonics, nanodevice creation, optoelectronics, data storage, and antibacterial applications[4]. Their applications, however, necessitate the capacity to generate narrow size distribution of silver nanoparticles on a supporting, with exact sizing and

dispersion control. Because Catalysts that work are permeable, it's difficult to say what influences size, shape, and dispersion of nanomaterials play in catalytic activity. Numerous historical techniques have been found for growing silver nanoparticles through spin coating followed by many agents of reduction like thermal reduction to explore the shape and size of Ag nanoparticles[5]. Some others used a different technique called the single-step method to synthesize Ag nanoparticles by using a particular plant as a reducing agent found naturally[6]. Moreover, silver nanoparticles were prepared chemically with variable sizes and shapes such as sodium hypoborate ($NABH_4$) as a reducing agent[7]. Nanomaterials are grown on a surface platform, However, they may be studied using microscopic and spectroscopic methods to determine the specific catalytic process[8]. Several methods have been investigated for the synthesis of silver nanoparticles including sputtering, metal vapor deposition, photochemical, sol-gel, chemical reduction, microwave-assisted synthesis, laser ablation, thermal decomposition, and ion implantation[4]. In terms of dependability, particle uniformity, easily adjustable spin coating parameters, and cost-effectiveness, spin coating is preferable to these approaches for growing supported monodispersed nanoparticles[9]. Surface activity and performance in targeted applications can be altered by altering stability, size distribution, and shape. Organic stabilizers can control particle shape and prevent particle

* Corresponding author

E-mail address: ari.yatem@uoz.edu.krd (Instructor).

Peer-reviewed under the responsibility of the University of Garmian.

agglomeration, but organic residues limit particle surface activity. A surfactant-free technique for the creation of supported silver (Ag – NPs) with fine growth control is needed to solve this problem[10]. This work investigates a surfactant-free technique for growing Ag thin film nanostructure on the surface of the glass through the spin-coating method in the solution of $AgNO_3$ and chemical elimination in watery sodium borohydride ($NaBH_4$), hydrazine hydrate (N_2H_4), and thermal reduction in the H_2 atmosphere.

2. Experimental work (Methodology):

The Ag thin film nanostructures were grown using only high purity ingredients. As a source of silver nitrate, $AgNO_3$ (Sigma Aldrich) was used, while analytical ethanol [purity 99.9%] served as the solvent.

($AgNO_3$) was used to create silver (Ag) thin films on glass substrates, three stages are involved in the spin coating synthesis of Ag thin films nanostructure as shown in figure 1:
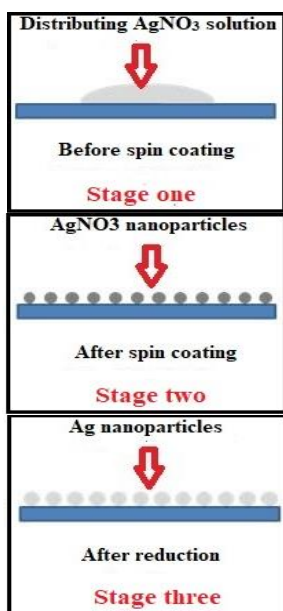

Figure 1: Three processes in the creation of Ag nanoparticles are depicted schematically in this diagram.

The first stage is to distribute the $AgNO_3$ ions solution. The second stage is to spin the substrate at an optimal RPM to obtain Ag thin film nanostructure and the reduction of $AgNO_3$ nanoparticles to formed Ag nanoparticles is the third stage. It's important to note that by adjusting variables from any of the processes, we may get metal nanoparticles with a variety of morphologies and sizes, as well as varied distributions[11]. If we modify the percentage of the volume of the $AgNO_3$ solution or add supplements in stage one, we may expect alteration in the growth process (i.e., shape, dispersion, and size) of metal nanoparticles (RPM, ramp, and time) in stage two, and change the reduction procedure in stage three. In this paper, we will look at phase three to see how the reduction mechanism influences the development process of nanomaterials. The reduction can be achieved chemically using a reductant or thermally in a reducing atmosphere. On a glass surface, a 0.01 M of $AgNO_3$ ethanolic solution with a volume of 100 µl was utilized in the spin coating technique. Before the deposition process, a glass substrate with a glass area of (2 x 2) Cm was cleaned and sonicated in water then rinsed with distilled water. The experimental work was done by spin coating technique with 2500 rpm for about 40 seconds. By immersing the deposited $AgNO_3$ nanoparticles in a 0.01 M aqueous hydrazine hydrate, sodium borohydride $NaBH_4$ for 90 seconds they were chemically diminished, and thermally by heating at 500 ∘C for 4 hours, immediately in the oven which was insulated from air cooling to room temperature in an H_2 atmosphere at one atmospheric pressure. X-ray diffraction (XRD) was used to characterize the thin films that had been created, and

Scanning Electron Microscope examined the morphology of the nanoparticles. Moreover, A UV-vis-NIR spectrophotometer was used to examine the optical properties of thin films produced on glass surfaces in the wavelength range of 300 to 750 nm.

3. Results and Discussion:

3.1 Analyzing the Thin Film Structure.

The prepared Ag thin films have been characterized using X-ray diffraction (XRD), using a Bruker D8 advanced diffractometer. Figure 2. illustrates the X-ray diffraction (XRD) structure of silver thin films deposited on glass substrates using hydrazine hydrate, sodium borohydride, and thermal reduction at a given $AgNO_3$ concentration. The diffraction peak was investigated and obtained the strong peak along the (111) plane at the value of 2θ (37.91), and some other diffraction peaks showed low intensity such as the (200) plane at the value of 2θ (44.22), (220) plane at the value of 2θ (64.60), as well as (311) plane at the value of 2θ (77.50). The four detected peaks of silver were all identical and compared with the standard powder diffraction card of Joint Committee on Powder Diffraction Standards (JCPDS) silver file No, (04 - 0783). This suggests that the silver thin films formed by spin coating were crystalline and had a face-centered cubic structure. The diffraction pattern revealed no further peaks of silver oxide or silver hydroxide, indicating that the film is entirely made of silver[12].
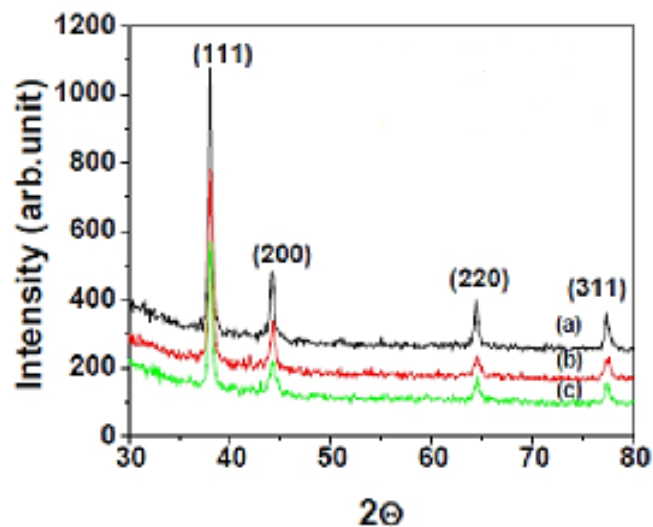

Figure 2: Depicted XRD structure of the deposited nanocrystalline silver thin film on the glass substrate obtained after immersing in liquid (a) hydrazine hydrate solution, (b) sodium borohydride, and (c) thermal reduction.

The crystallite size (D) of the Ag thin film nanostructure for the peak diffractions including (111), (200), (220), and (311) planes have been calculated by the Sherrer formula[13], as shown in table (1).

$$D = \frac{K \lambda}{\beta \cos \theta}$$

Where (D) is the crystallite size in nm, (K) is the Sherrer constant (0.68 to 2.08) we selected (0.9) for spherical crystallites with cubic symmetry, (λ) is the X-Ray source wavelength Cu Kα =

1.5406 A°, (β) is the line broadening at full width half maximum (FWHM) in radians,

(θ) is the Braggs angle in degrees, half of 2θ.

Table 1: Shows the analysis of Silver thin film nanostructure.

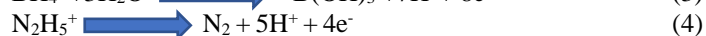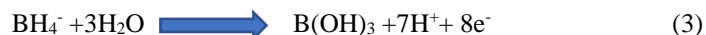| Peak Diffractions	2θ	FWHM	Crystallite size (D) in nm	The average crystallite size (D_{ave}) in nm
(111)	37.91	0.3727	21.4	
(200)	44.22	0.5445	14.6	22.45
(220)	64.60	0.4364	28.7	
(311)	77.50	0.6356	25.1	

3.2 Morphological Analysis.

The surface topography of the Ag nanoparticles was examined by JEOL JSM-6360A (SEM) at an operating voltage of 20 kV. Scanning Electron Microscope (SEM) pictures of Ag thin films generated through the spin coating and silver nanoparticles acquired through the chemical reduction in liquid $NaBH_4$, hydrazine solution, and thermal reduction of $AgNO_3$ nanoparticles on the surface of the glass are shown in Figure 3. The development of a thin liquid layer of uniform thickness emerges from spin coating $AgNO_3$ solution over a glass surface. Furthermore, spinning causes the ethanol in this film to evaporate, resulting in $AgNO_3$ nanoparticle coatings growing on the substrate. Excess growth of Ag thin films on glass surfaces results in uniform covering as we can see in Figure 3a, These $AgNO_3$ nanoparticles are reduced to Ag nanoparticles.

It is commonly understood that rapid nucleation, as compared to growth, leads to tiny particle sizes, and conversely. Redox reactions occur in the creation of nanomaterials via chemical reduction, with metal M^{n+} ion species being reduced to M^o and the reducing X^m agent being oxidized as follows[14].

$$M^{n+} + n e^- \longrightarrow M^o \qquad (1)$$
$$X^m + n e^- \longrightarrow X^{m-n} \qquad (2)$$

The following are the oxidation reactions of BH_4 and N_2H_5+ ions formed by dissociating $NaBH_4$ and N_2H_5 in water, respectively.

$$BH_4^- + 3H_2O \longrightarrow B(OH)_3 + 7H^+ + 8e^- \qquad (3)$$
$$N_2H_5^+ \longrightarrow N_2 + 5H^+ + 4e^- \qquad (4)$$

The typical reduction potential determines the intensity of the reducing agent; the strength of the reducing agent increases with increasing negative potential; pH also influences reduction. The diminution rate of $AgNO_3$ in $NaBH_4$ is quicker than hydrazine hydrate, as evidenced by the reduction potentials of $BH_4^{-\,(-0.481V)}$ and $N_2H_5^{+(-0.23V)}$ ions. In other words, when Ag nanoparticles are reduced in $NaBH_4$, the nucleation rate is greater than when Ag nanoparticles are reduced in hydrazine hydrate, resulting in smaller Ag nanoparticles, as we can see in both figures (3b – 3c). Following chemical reduction with $NaBH_4$ and Hydrazine hydrate, the distribution of particle size is detected un uniform Ag nanoparticles, however, during thermal reduction, the distribution of particle size is obtained as uniform Ag nanoparticles, demonstrating the excellent method and technique. Thermal reduction differs from the chemical reduction in taking the benefit of thermal energy to help decrease Ag nanoparticles diffuse, as a result, Ag nanoparticles uniformly dispersed as shown in fig. 3d.
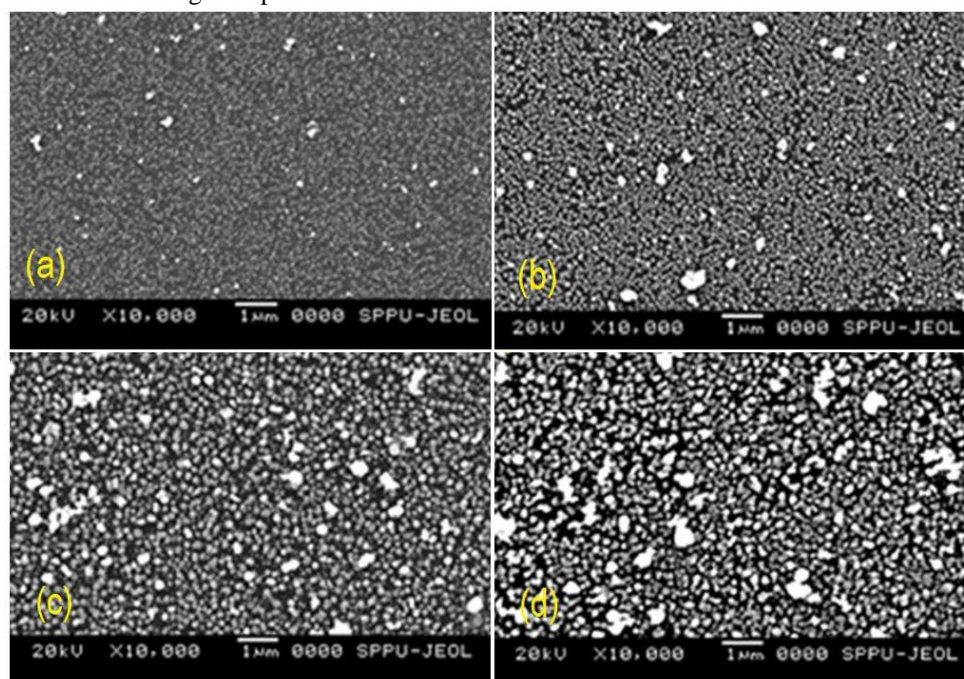

Figure 3: Shows SEM pictures of (a) spin-coated AgNO3 nanoparticle films, and silver nanoparticles generated after chemical reduction in liquid phase (b) NaBH4, (c) hydrazine hydrate solution, and (d) thermal reduction.

3.3 Optical properties.

A UV-vis-NIR spectrophotometer was used to verify the growth of Ag thin films with the help of JASCO V-670 UV- vis – NIR ranges between (300 nm – 750 nm) wavelength. The absorption spectra of $AgNO_3$ and silver nanoparticles produced through reductions in chemical aqueous $NaBH_4$, Hydrazine hydrate, and thermal reduction in the H_2 atmosphere are shown in Figure 4. Noble-metal nanoparticles feature exceptional size-dependent optical characteristics, with a prominent UV-visible extinction band that contrasts with the bulk metal's spectrum. When the incoming photon frequency resonates with the group excitation of the conduction electrons, an extinction band known as the localized surface plasmon resonance (LSPR) is detected[15]. The interparticle spacing of the nanoparticle, size, and shape, as well as its dielectric characteristics and those of its nearby environment, including the substrate, solvent, and adsorbates, are all known to influence the peak due to LSPR in the absorption spectrum. The presence of LSPR peaks as we can see in Figure 4 suggests that Ag nanoparticles were formed as a result of the reduction of $AgNO_3$ particles, which had no LSPR peak. Because of the variation in the reduction process, there is a change in peak location and a shift in intensity. When we compare the solution of hydrazine with the aqueous $NaBH_4$, the LSPR peak is somewhat red shifted; however, there is a large redshift for Ag nanoparticles formed through thermal reduction when we compared it with other reductions. The optical studies are congruent with the SEM findings since changes in particle size, shape, and distribution generate variations in intensity and peak location[16].
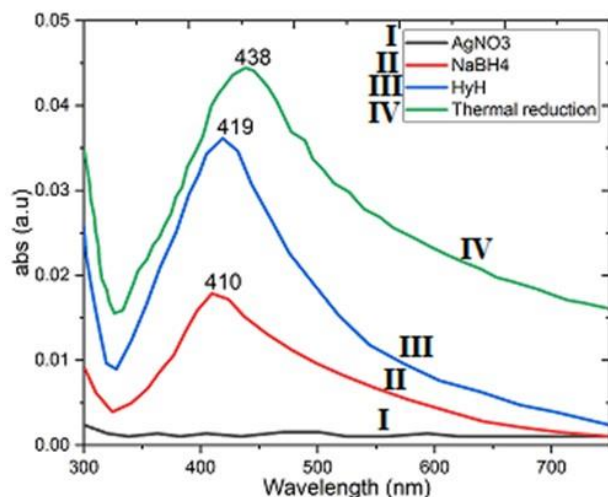

Figure 4: Shows UV-Vis-NIR absorption spectra of (I) $AgNO_3$ nanoparticle thin films, and silver nanoparticles generated after chemical reduction in liquid phase (II) NaBH4, (III) hydrazine hydrate solution, and (IV) thermal reduction.

Conclusion

In the research, we have showed how Ag nanoparticles could be produced on the surface of glass via spin coating of $AgNO_3$ solution proceeded by thermal and chemical reduction, which may be employed for concept catalytic research. By altering the reaction mechanism, the shape, dispersion of Ag nanoparticles, and size may be changed. The XRD results have shown the identical diffraction peaks of silver, which means the formed thin films were crystalline and have had a face-centered cubic structure. Moreover, the crystallite structure (D) itself has proven the Ag thin film nanostructure. The localized surface plasmon resonance LSPR peaks recorded for Ag nanoparticles vary in strength and location depending on the reduction procedure. We discovered that thermal reduction in an H_2 atmosphere is a superior reduction procedure to chemical reduction for getting evenly dispersed spherical Ag nanoparticles.

Conflict of interests

None

References

1. Nagarajan, Ramanathan, and T. Alan Hatton, eds. Nanoparticles: synthesis, stabilization, passivation, and functionalization. American Chemical Society, 2008.
2. Chouhan, Neelu. "Silver nanoparticles: Synthesis, characterization and applications." (2018).
3. Ju-Nam, Yon, and Jamie R. Lead. "Manufactured nanoparticles: an overview of their chemistry, interactions and potential environmental implications." *Science of the total environment* 400, no. 1-3 (2008): 396-414.
4. Pozo, David, ed. *Silver nanoparticles*. BoD–Books on Demand, 2010.
5. Ansari, A. A., and S. D. Sartale. "Narrow size distributed Ag nanoparticles grown by spin coating and thermal reduction: Effect of processing parameters." *Materials Research Express* 3, no. 8 (2016): 085023.
6. Rodríguez-León, Ericka, Ramón Iñiguez-Palomares, Rosa Elena Navarro, Ronaldo Herrera-Urbina, Judith Tánori, Claudia Iñiguez-Palomares, and Amir Maldonado. "Synthesis of silver nanoparticles using reducing agents obtained from natural sources (Rumex hymenosepalus extracts)." *Nanoscale research letters* 8, no. 1 (2013): 1-9.
7. Amany, A., Sanaa F. Gad El-Rab, and F. Gad. "Effect of reducing and protecting agents on size of silver nanoparticles and their anti-bacterial activity." *Der Pharma Chemica* 4, no. 1 (2012): 53-65.
8. McConnell, Wyatt P., James P. Novak, Louis C. Brousseau, Ryan R. Fuierer, Robert C. Tenent, and Daniel L. Feldheim. "Electronic and optical properties of chemically modified metal nanoparticles and molecularly bridged nanoparticle arrays." *The Journal of Physical Chemistry B* 104, no. 38 (2000): 8925-8930.
9. Zhang, Zhi, Wenfei Shen, Jing Xue, Yuanmeng Liu, Yanwei Liu, Peipei Yan, Jixian Liu, and Jianguo Tang. "Recent advances in synthetic methods and applications of silver nanostructures." Nanoscale Research Letters 13, no. 1 (2018): 1-18.
10. Ansari, A. A., and S. D. Sartale. "Controlled growth of thermally stable uniform-sized Ag nanoparticles on flat support and their electrochemical activity." Applied Physics A 119, no. 2 (2015): 503-516.
11. Mallory, Glenn O., and Juan B. Hajdu, eds. *Electroless plating: fundamentals and applications*. William Andrew, 1990.
12. Diantoro, Markus, Alif Fitria Chasanah, Nandang Mufti, and Abdulloh Fuad. "Fabrication of Silver Nanoparticles and Its Films and Their Characterization of Structure and Electrical Conductivity." In *Advanced Materials Research*, vol. 896, pp. 341-346. Trans Tech Publications Ltd, 2014.
13. B.D. Cullity, Elements of diffraction, Addison-Wesley publishing-company inc.(1978).
14. Cushing, B. L., Kolesnichenko, V. L., & O'connor, C. J. (2004). Recent advances in the liquid-phase syntheses of inorganic nanoparticles. Chemical Reviews, 104(9), 3893–3946.
15. Petryayeva, Eleonora, and Ulrich J. Krull. "Localized surface plasmon resonance: Nanostructures, bioassays and biosensing—A review." *Analytica chimica acta* 706, no. 1 (2011): 8-24.
16. Smitha, S. L., Nissamudeen, K. M., Philip, D., & Gopchandran, K. G. (2008). Studies on surface plasmon resonance and photoluminescence of silver nanoparticles. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 71(1), 186–190.