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Deposition and Characterization Of Nanocrystalline Silver Thin Films By Using SILAR Method

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Abstract. Nanocrystalline silver thin films were deposited on glass substrate by using Successive Ionic Layer Adsorption and Reduction (SILAR) method. Silver nitrate and hydrazine hydrate (HyH) were used as precursors. The deposited silver thin films were characterized by using X–ray diffraction (XRD), UV-visible-NIR absorption spectroscopy and scanning electron microscopy (SEM) techniques. Effect of concentration of HyH on properties of SILAR grown silver thin films has been extensively studied.

Keywords: Silver, Surface plasmon resonance, SILAR.
PACS: 61.05.cp, 68.37.HK, 68.55.A, 78.40.Kc, 81.16.Be, 81.07.Bc.

INTRODUCTION

Owing to the unique optical property to show surface plasmon resonance, metal nanoparticles have various applications in photocatalysis, solar cells, etc. [1] Silver nanostructures have various industrial applications [2, 3]. There are various methods for the formation of metal nanostructures.

In the present work we have deposited nanocrystalline silver thin film on glass substrates by using SILAR method. Y. F. Nicolau has invented successive ionic layer adsorption and reaction (SILAR) method for semiconductor thin film deposition, since then it has been used to grow different semiconductor and oxide thin films [4]. However, very few reports are available for metal thin film deposition using SILAR, where reaction step is nothing but reduction of metal ions to get metal films [5]. In SILAR thickness and other properties of the films can be easily controlled by changing the precursors characteristics (concentration, pH and temperature), immersion (adsorption, reduction and rinsing) time and the number of deposition cycles [4].

EXPERIMENTAL DETAILS

Silver thin films were deposited on glass substrates by using silver nitrate and hydrazine hydrate (HyH) as precursor solutions. In this case concentration (conc.) of HyH was varied from 1M to 0.01M at fixed conc. of $AgNO_3$ (0.01M). A deposition cycle of silver thin film consists of four steps. First the substrate was immersed in $AgNO_3$ solution for 10 sec. Then the substrate was rinsed in distilled water for 30 sec to remove excess unadsorbed Ag^{2+} ions. After that the substrate was immersed in HyH solution for 10 sec. In the last step the substrate was again rinsed in distilled water for 30 sec to remove excess HyH. The deposition cycles were repeated for different number of times. The prepared thin films were characterized by means of X-ray diffraction (XRD), using a Bruker D8 advance diffractometer. Optical absorption measurements were carried by JASCO UV-Vis-NIR spectrophotometer. Scanning electron microscopy (SEM) images were recorded using a JEOL JSM-6360A microscope with operating voltage 20 kV.

RESULTS AND DISCUSSION

Fig. 1 shows the XRD pattern of silver thin films deposited on glass substrates using different conc. of HyH solutions at fixed $AgNO_3$ conc. (0.01M). All the observed four peaks (111), (200), (220), (311) were exactly matching with the standard JCPDS data for silver. This indicates that SILAR deposited silver thin films were crystalline with face centered cubic structure. No additional peaks of silver oxide or silver hydroxide were observed in the diffraction pattern, so it is confirmed that the film is of silver only.

Fig. 2 shows the optical absorption spectra of silver thin films deposited on glass substrates using solution of different HyH conc. (0.01M to 1M) at fixed $AgNO_3$ conc. (0.01M). From these spectra it is observed that surface plasmon peak appeared in the

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region from 384 to 419 nm can be assigned to dipole Plasmon band of nanocrystalline silver.

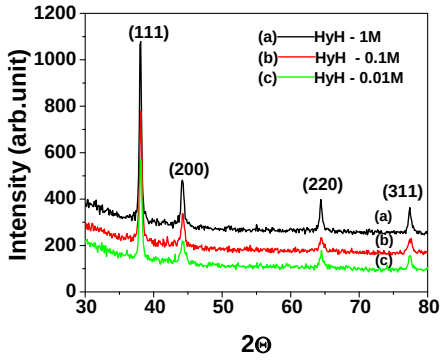

FIGURE 1 XRD patterns of nanocrystalline silver thin films deposited on glass substrates using various conc. of HyH at fixed $AgNO_3$ conc. (0.01M).

UV-Vis absorption spectra reveals that as concentration of HyH increases intensity of SPR peak increases. SPR lies in the range of 384 nm to 419 nm.

This phenomenon can be explained from the influence of reduction rate on the nucleation. The number of nuclei formed in the beginning of the reduction determines the number and size of the resultant particles. At low conc. of HyH because of low rate of reduction initially few nuclei were formed on the substrate, which further grows leading to larger particle size. On the contrary, as the conc. of HyH increases because of higher rate of reduction excess number of nuclei was formed results into formation of smaller silver nanoparticles which were agglomerated further.

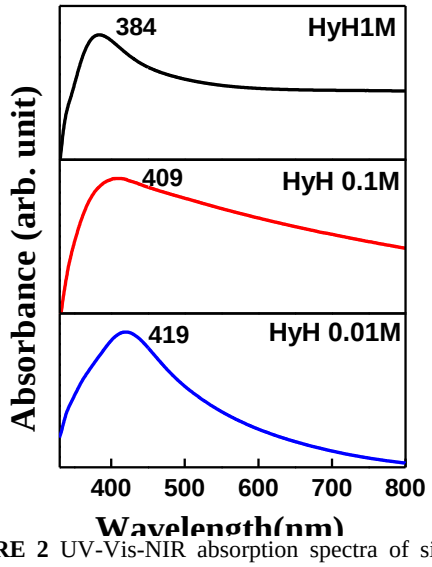

FIGURE 2 UV-Vis-NIR absorption spectra of silver thin films at various conc. of HyH at fixed $AgNO_3$ conc. (0.01M)

Fig. 3 shows typical SEM images of silver thin film on glass substrate at fixed conc. of $AgNO_3$ (0.01M) and HyH (0.1M). It is observed from Fig 3(a) that the particles are uniformly distributed over the glass substrate. Higher magnification reveals (Fig. 3(b)) the nanocrystalline nature of the silver film. The size of the silver grains was found to be in the range 40-50 nm. No significant difference in grain size was observed by varying HyH concentration.

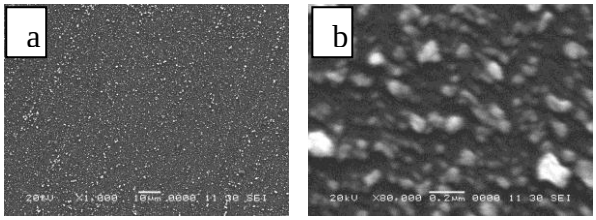

FIGURE 3 SEM images of silver thin film at fixed concentration of $AgNO_3$ (0.01) and HyH (0.1M)

CONCLUSIONS

In the present work nanocrystalline silver thin films are successfully deposited by SILAR method using solution of $AgNO_3$ and HyH as precursors. XRD confirmed the formation of nanocrystalline silver with face centred cubic structure. UV-Vis absorption spectra reveals that as concentration of HyH increases intensity of SPR peak increases, mainly due to diffrence in nucleation and growth behaviour. SEM shows uniformaly distributed silver nanoparticles of size 40-50nm.

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