J. Min. Metall. Sect. B-Metall. 49 (1) B (2013) 91 - 95

Journal of Mining and Metallurgy,
Section B: Metallurgy

SEM/EDX AND XRD CHARACTERIZATION OF SILVER NANOCRYSTALLINE THIN FILM PREPARED FROM ORGANOMETALLIC SOLUTION PRECURSOR

R. Dimitrijević[a,+], O. Cvetković[b], Z. Miodragović[b,c], M. Simić[d], D. Manojlović[b,c], V. Jović[e,*]

[a] Faculty of Mining and Geology, Department of Crystallography, University of Belgrade, Serbia
[b] Center of Chemistry, Institute of Chemistry, Technology and Metallurgy, University of Belgrade, Serbia
[c] Faculty of Chemistry, University of Belgrade, Serbia
[d] Center of New Technologies (CNT), Belgrade, Serbia
[e] Center of Microelectronic Technologies, Institute of Chemistry, Technology and Metallurgy, University of Belgrade, Serbia

(Received 11 January 2012; accepted 19 November 2012)

Abstract

The Ag nano-structured thin films prepared on flat glass substrates have been studied. The ball-like silver nanoparticles have been synthesized in large quantity by using a modified method of hydrolytic decomposition of silver complexes with amino types ligands formed in ethanol aqueous solution. SEM analysis revealed that Ag nanoparticles are all sphere shaped with bimodal size (40 and 70 nm) distribution. The results of XRD powder pattern examination show that Ag nanoparticles are pure phase, well crystallized. The unit cell dimensions measured on synthesized Ag nano films show small but frequent contraction in comparison to Ag metal standard.

Keywords: *Ag nanoparticles; Sphere shaped; Chemical deposition; XRD technique; SEM/EDX analysis*

1. Introduction

Recently there have been reported a huge variety of methods of preparation of nanostructured noble metal materials consisting of very small (diameter between 2 and 100 nm) metallic particles [1]. Depending on the nature of nanoparticles i.e. their structural and textural characteristics, these material posses interesting electronic, optical, magnetic, catalytic and other properties that can be tailored regarding a function of particle size and shape [2]. According to their unique properties discussed materials are suitable for novel applications in the fields of catalysis, microelectronics, optoelectronics, biomedicine, etc. [3-5]. There are numerous methods and techniques for deposition of noble metals in thin films forms on substrate, such as physical and chemical vapor deposition [6-10], electrochemical deposition [11-13], chemical bath deposition [14], mechanochemical and thermal deposition [15] and many others. Among all of them, there is little doubt that chemical bath deposition from organometallic solutions [16-18] as noble metals precursors is the simplest and probably the most economical one.

Bearing in mind the importance of nanostructured materials in modern technology, the CNT company developed a suitable, slightly modified chemical technique for fabrication of Ag nanostructured thin film on various substrates. Moreover, the thickness of Ag thin film, as well as the size of a particle, obtained by this technique can be easily tailored. Being interested in catalytic properties of nanostructured noble metals, as the possibility of improvement of the current cleaning treatment of the refinery waste water [19], in this paper we report the result of SEM/EDX and XRD characterization of CNT diverse nanostructured Ag thin films deposited on flat glass carriers.

2. Experimental procedure

The production of material analyzed is based on a modified method of hydrolytic decomposition of silver complexes with amino type ligands formed in ethanol-aqueous solutions [19, 20]. This technique is simple and does not require any special equipment or setup. Several samples with different thickness of Ag film deposited on glass carriers have been obtained.

[+] *Prof. Dr Dimitrijević passed away before submission of this paper. We dedicate this publication to his memory*

* *Corresponding author: vjovic@nanosys.ihtm.bg.ac.rs*

DOI:10.2298/JMMB120111041D

Glass carriers are square plates 15 x 15 mm, with uniform thickness and silver films are deposited from above mentioned solutions by chemical reduction using formaldehyde. The obtained silver films were prepared from starting solutions with different concentrations of silver salts (1-15 % w/w of Ag^+ ions).

The microstructure and composite homogeneity of the obtained samples were investigated using a SEM/EDX scanning microscope JEOL-JSM 64000 LV. Energy dispersive X-ray analysis measurements were performed under standard conditions.

The X-ray powder diffraction (XRD) patterns were recorded on a Philips PW-1710 automated diffractometer using a Cu tube operated at 40 kV and 30 mA. The instrument was equipped with a diffracted beam curved graphite monochromator and Xe-filled proportional counter. Diffraction data were collected in the range 2q Bragg angles, 4-130 °, counting for 0.4 (routine phase identification) and 4.0 seconds (unit cell and crystallite dimensions measurements) at 0.02 ° steps, respectively. A fixed 1 ° divergence and 0.1 mm receiving slits were used. A 0.5 mm thick ribbon of pure Ag metal, prepared by the melt spinning method, was used as a test sample in our research. Silicon powder was applied as a standard calibration of diffractometer. All XRD measurements were recorded at ambient temperature. The unit cell dimensions of prepared Ag particles were calculated from XRD powdered data by last square refinement procedure using the program Lsucripc [21]. The cubic unit cell dimensions and Fm3M (225) space group given by Swanson and Tatge [22] were applied as a starting parameters for least square fitting approach in Rietveld refinement [23] procedure. Crystallite size dimensions i.e. the length of coherent ordered structure, $<D_{hkl}>$, were determined by using an interactive Windows program for profile fitting and size analysis Winfit [24]. Full width at half-maximum (FWHM) values of the(111) peak having 2.359 Å distance was fitted assuming pseudo Voight profile.

3. Results and Disscusion

3. 1. SEM/EDX investigations

Figure 1 (a-d) shows the SEM images of synthesized thin films prepared from different concentration Ag-organometallic precursors, respectively. It is clear from these images that a common characteristic of the particles is their spherical shape.

It is also visible that particles are mutually different in size varying between 30 to 140 nm with preferred bimodal (40 and 70 nm) distribution, shown on (Fig. 2.) for nano-film which was grown from the solution with concentration of 15 % w/w Ag^+. Similar particle size distributions are obtained in other films with nanosized Ag particles deposited from solutions with different Ag^+ concentrations.

Also, the particles complied with the principle of the most dense sphere packaging. However, it is not possible to recognize if either type FCC or HCP is present [2, 3]. The particles´ sphere shape was observed by Z. Wang at al. [25], who by TEM investigations show that the spheres are actually the Ag single crystals with developed (111) and (100)

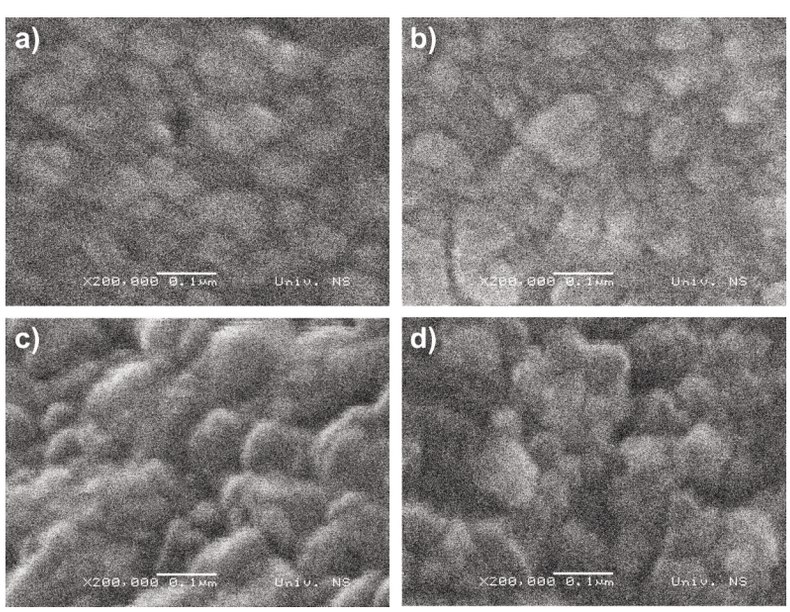

Figure 1. *The SEM images of Ag-nanostructured thin films obtained from solutions with different organometallic precursors concentrations: a) 2 % w/w Ag^+; b) 5 % w/w Ag^+; c) 8 % w/w Ag^+; and d) 15 % w/w Ag^+.*

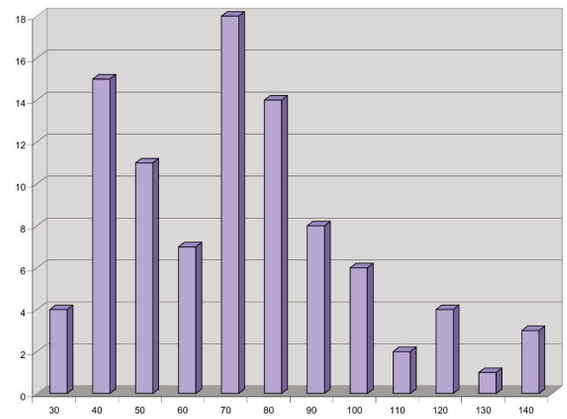

Figure 2. *The Ag-nano particle size distribution histogram (X – axis - particles´ dimensions; Y - axis – abundance) obtained by measurements of spheres for film morphology shown in Fig. 1. d. Film was deposited from solution with 15 % w/w Ag^+ concentration.*

facets [2]. Accordingly, it may be considered that the Ag spheres observed are single crystals, too. Regarding Ag nano particles size distribution, it seems that it is a random process, which is not dependent on concentration of Ag^+ ions in the solution. However, a thickness of deposited Ag thin film is strongly dependent on silver concentration in the solution from which growth was performed. This is evident from spot EDX (Energy-dispersive X-ray spectroscopy) spectra measurements (Fig. 3.), which were obtained from the samples shown in Fig. 1, respectively.

A progressive increase of intensities of AgL spectra lines (spectra a to d, in Fig. 3.) are consistent with preparation procedure. The only difference between growth conditions of films, whose EDX spectra are shown on Fig. 3, is concentration of Ag^+ ions in the solution. The measured Ag spectra line becomes more intense in films obtained from solutions with higher Ag^+ concentration. It is also important to notice that line EDX analysis in different samples shows chemical homogeneity of Ag films. It is known from scientific literature that intensities of any spectral lines in EDX analysis are proportional to element abundance. Given that EDS method cannot distinguish between elemental Ag and Ag atoms in other compounds, this result only illustrates the increase of the Ag concentration in the nano-films. Increased intensity of Ag line is attributed to the increased content of silver in the nano film.

3. 2. X-ray powder diffraction investigations

XRD powder patterns of Ag-nano thin films deposited on flat glass carriers are shown in Fig. 4. In this figure the powder patterns are arranged in an increasing order from very low (curve a) to the highest Ag concentration (curve f). The curve designated with the letter g shows a powder pattern of pure Ag-ribbon which is used for comparison. As seen in Fig.4, the basic characteristic of investigated thin films is the presence of pure Ag crystalline phase which is detected in all samples. As a proof for this conclusion, which is opposite to the published [26]

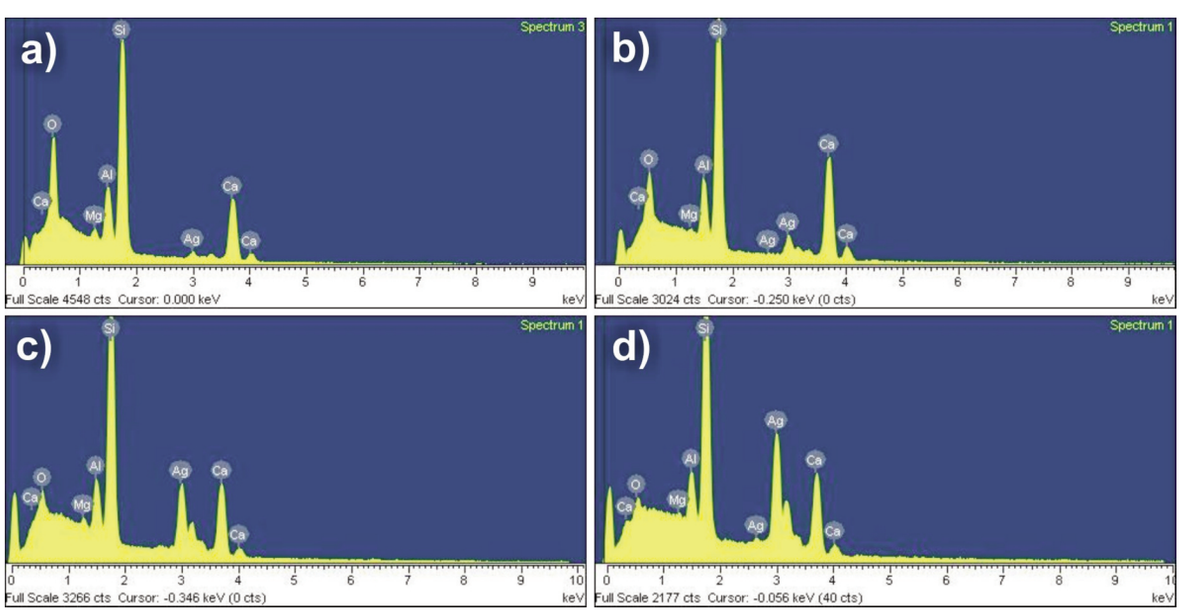

Figure 3. *The spot EDX spectra of Ag-nanostructured thin film samples shown on Figure 1. Glass coated with Ag-nanostructured film deposited from solution with: a) 2 % w/w concentration of Ag^+; b) 5 % w/w concentration of Ag^+; c) 8 % w/w concentration of Ag^+ and d) 15 % w/w concentration of Ag^+.*

results on AgO and Ag_2O simultaneous deposition from Ag^+-triethanolamine, we enclose the Rietveld refinement plot of a sample coated with film deposited from the solution with 15 % Ag concentration, Fig. 5.

Other crystallographic characteristics, such as unit cell dimensions and grain size measurements, are summarized in Table 1.

The color of samples observed by naked eye is noticed, as well. It is obvious from Table 1 that measured unit cells of Ag-nanostructured thin films are frequently smaller than JCPDS Ag standard. Although we have no rational explanation for the observed difference, we believe that our measurement represents the first experimental evidence on unit cell concentration in Ag-nanoparticles. It is also interesting that due to XRD measurements the average grain size of 18 nm is obtained. This is several times smaller than particle sizes observed by SEM investigations (Fig. 1. and Fig. 2.). The observed difference can be attributed to the fact that XRD measurements consider crystallite sizes as sizes of "coherently diffracting domains" of crystals while grains may contain several of these domains. Another reason for these differences could be a possible plasmon [27] interaction of SEM electron bundle with Ag-nano particle surface, which appears in magnification size effect. The true size and shape of prepared Ag-nano particles could be determined by TEM investigation, which will be the subject of another paper of ours.

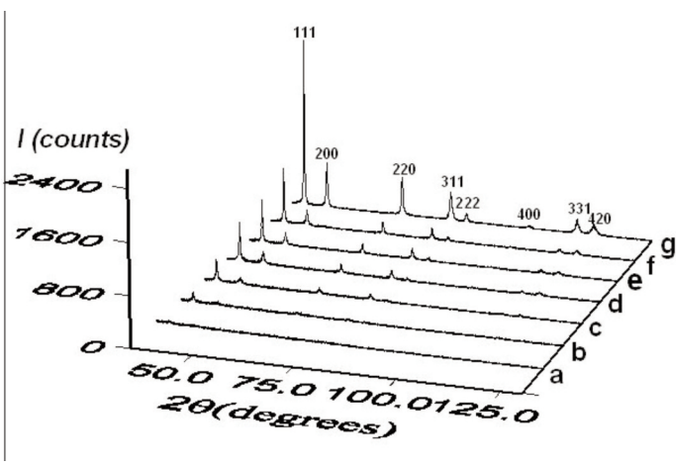

Figure 4. *The XRD powder patterns of Ag- nanostructured film deposited on flat glass carriers. Depositions are performed from solutions with different Ag^+ concentrations: a) 1 % w/w; b) 2 % w/w; c) 5 % w/w; d) 8 % w/w; e) 12 % w/w and f) 15 % w/w. g) a powder pattern of pure Ag-ribbon used as standard. Numerals on the top of each peak (curve g) designate a Miler indices of characteristic distances.*

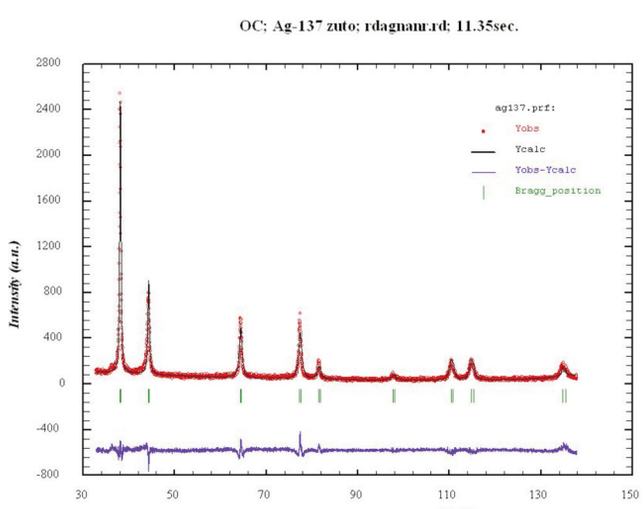

Figure 5. *Rietvald refinement plot of nanosilver thin film on glass carrier deposited from the solution with 15 % w/w Ag^+ concentration.*

Table 1. *XRD and color characteristics of nanosilver thin films deposited on glass carriers from solutions with various concentrations of Ag^+ (in % w/w).*

Ag^+ concentration	Sample color (by eyes)	Cubic lattice constants (Å)	Peak width at half max. $FWHM_{(111)}$	Crystallite size dimensions $<D_{111}>$ nm
1	Black	Not measured	Not measured	Not measured
2	Black to brown	4.081	0.505	13
5	Brown	4.083	0.445	14.4
8	Light yellow	4.082	0.373	17.6
12	Light yellow	4.0814	0.329	20.5
15	Light yellow	4.0808	0.302	22.6
Ag-ribbon	Light grey	4.0873	Not measured	Not measured
JCPDS		4.0863		
4-0783				

4. Conclusions

In summary, a ball or sphere-like pure silver nanoparticles thin films have been prepared in large scale by using a simple Ag-organometallic solution-phase approach. Size measurements (SEM/EDX) show a bimodal distribution of Ag-nano particles (40 and 70 nm). XRD particle size measurements show that small particles are the most frequent in distribution. SEM/EDX investigations indicate that the thickness of deposited Ag-nanostructured thin film is proportional to the Ag concentration in a solution.

Acknowledgement

This work was supported by grants from the Government of the Republic of Serbia – Ministry of Education and Science, Grant No. 172030, 176006 and TR 32008. The authors also wish to thank to Dr M. Bokorov from the University of Novi Sad, Department for Biology and Ecology for SEM/EDX scanning.

References

1. Springer Handbook of Nanotechnology (Bharat Bhushan, Editor), Springer, New York, 2007.
2. Z. Wang, J. Phys. Chem., B104 (2000) 1153-1175.
3. M. Brust, C. J. Kiely, Colloids Surf., A, 202 (2002) 175-186.
4. E. Hutter, J. Fendler, Adv. Mater., 16 (19) (2004) 1685-1706.
5. V. Ćosović, N. Talijan, D. Živković, D. Minić, Ž. Živković, J. Min. Metall. Sect. B-Metall., 48 (1) B (2012) 131-142.
6. C. Rao, G. Kulkarni, P. Thomas, P. Edwards, Chem. Soc. Rev., 29 (2000) 27-35.
7. R. Devenish, T. Goulding, B. Heaton, R Whyman, J. Chem. Soc., Dalton Trans., (1996) 673-679.
8. N. Arul Dhas, N. Cohen, A. Gedenken, J. Phys. Chem. B, 101 (1997) 6834-6838.
9. N. Arul Dhas, A. Gedanken, J. Mater. Chem., 8 (1998) 445-450.
10. A. Henglein, J. Phys. Chem., 97 (1993) 5457-5471.
11. M. Reetz, W. Helbig, J. Am. Chem. Soc., 116 (1994) 7401-7402.
12. M. T. Reetz, S. A. Quaiser, M. Winter, J.A. Becker, R.Schiifer, U. Stimming, A. Marmann, R. Vogel, T. Konno, Angew. Chem. Int. Ed. Engl., 35 (18) (1996) 2092–2094.
13. J. Sopousek, J. Bursik, J. Zalesak, Z. Pesina, J. Min. Metall. Sect. B-Metall., 48 (1) B (2012) 63-71.
14. M. Reetz, M. Winter, R. Breinabauer, T. Thurn-Albrecht, W. Vogel, Chem. Eur. J., 7 (2001) 1084-1094.
15. J. Thomas, J. Appl. Phys., 37 (1966) 2914-2916.
16. C. Griffiths, H. O'Horo, T. Smith, J. Appl. Phys., 50 (1979) 7108-7115.
17. T. Tano, K. Esumi, K. Meguro, J. Colloid Interface Sci., 133 (1989) 530-533.
18. H. Ishizuka, T. Tano, K. Torigoe, K. Esumi, K. Meguro, Colloids and Surfaces, 63 (3-4) (1992) 337-340.
19. O. Cvetković, S. Nikolić, M. Simić, D. Manojlović, S. Hadži-Perić, Sixth International Symposium & Exhibition on Environmental Contamination in Central & Eastern Europe and the Commonwealth of Independent States, Prague, Czech Republic, Book of Abstracts, (2003) p. 171.
20. G Cardenas-Trivino, V Vera L, C Muñoz, Mater. Res. Bull., 33 (4) (1998) 645-653.
21. R. R. Garvey, Powder Diffr., 1 (1986) 114-116.
22. JCPDS data base. Card No.4-0783.
23. J. Rodrigez-Carvajal, Collected Abstract of Powder Diffraction Meeting, Toulouse (1990) p. 127.
24. S. Krumm, Materials Science Forum, 228-231 (1996) 183-190.
25. Z. L. Wang, S. A. Herfenist, R. L. Whetten, J. Bentley, N. D. Evans, J. Phys. Chem. B, 102 (17) (1998) 3068-3072
26. T. Kocareva, I. Groydanov, B. Pejova, Mater. Lett., 47 (6) (2001) 319-323.
27. A. Chhatre, P. Solasa, S. Sakle, R. Thaokar, A. Mehra, Colloids Surf., A, 404 (2012) 83-92.