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Coating Ag_2S Films on Silver Jewelry by Electrochemical Method

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Abstract

Ag_2S films were fabricated on the silver surface by electrochemical deposition from the mixture electrolyte solution including Sulfur and Sodium Hydroxide at room temperature. The composition and surface morphology of the Ag_2S films were investigated with various voltage from 1.50 V and 2 V for 30 – 150 s. The SEM images show that Ag_2S films are uniform with high compact at 1.50 V for 150 s. Moreover, the density of film tends to increase as the deposition time of immersion in electrolyte solution increases, and applied voltage up to 2 V. The AFM images show that the grain size and root mean square (RMS) roughness decrease with the increase of voltage value and deposition time of immersion. The CIE Lab results were showed that the color of Ag_2S films could be changed color from red-blue to dark-yellow-green. The applied voltage and deposition time are 1.50 V at 150 s, respectively for depositing Ag_2S films on the silver jewelry products.

Keywords: Jewelry; Silver; Electrochemical; Coating; Ag_2S

Introduction

Silver is a precious metal highly favored from ancient times until now a days. There are several studies about the combination of chemical and physical characteristics with the beauty of its surface appearance, making it an ideal material for producing decorative jewelry [1]. Silver has been investigated for various uses in industrial activities including the production of catalyst, antimicrobial material, electronic devices, electroplating, nanotechnology and jewelry [2]. Its excellent properties including ductility, malleability, luster, antimicrobial, corrosion and oxidation resistance, electrical and thermal conductivity. Generally, silver alloys consist of other metals to increase hardness, and reduce the amount of silver used. In the jewelry process, the silver alloys are called “sterling silver” (92.50% Ag, 7.50% Cu), “coin silver” (90% Ag, 10% Cu), and “brazing filler” (70% Ag, 30% Cu).

Thailand is recognized as one of the world's major gem and jewelry centers. In recent years, Thailand has increased the export of silver jewelry to German, Austria, China and Hong Kong. However, the jewelry products have developed the coating process on the surface of jewelry including electroplating [3] electrochemical [4], and painting. Therefore, all these industrial activities have been coated the silver to protect tarnished and color after finish process. Rhodium is used in the jewelry industry to enhance the appearance of other metals such as silver and white gold [5]. Black rhodium is not a naturally occurring metal. It is a proprietary alloy that combines rhodium with other metals to create a signature gunmetal look. Black rhodium plated jewelry was interesting and expensive for gems and jewelry designer.

In this study, the Ag_2S films was coated by means of an electrochemical cell of silver/silver in an electrolyte of Sulfur and Sodium Hydroxide. The coated surface of silver was also investigated. The films were created the pattern of black color on the silver ring, chain products.

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Materials and Methods

Silver ingots were prepared by casting process in the induction furnace under Argon atmosphere. The silver sheet was using rolling mill machine at 2 × 1 × 0.10 cm^3 in diameter. The silver samples were grounding up to 1,200 with SiC paper and then ultrasonically cleaned in acetone and deionized water (Fig.1). In the electrochemical process, we have procured following materials: Sulfur (S) and Sodium Hydroxide (NaOH) were bought from Sigma Aldrich Pvt. Ltd. Electrolyte solution was used at concentration of Sulfur: Sodium Hydroxide: DI water (1:2) with a liquor ratio of 1:100 and magnetic stirring at 90 °C for 1 h. The electrochemical cell was connected to the silver electrode with DC power apply HY3005 shown in Fig. 2. The electrochemical process of silver was controlled with applied voltage varied from 1.50 – 2 V, the current density is 50 A m^{-2} for 30, 60, 90, 120 and 150 s, respectively. Deposition of silver sulfide occurred by the following reaction scheme to equation (1) and (2);

$$3S + 6NaOH \rightarrow 2Na_2S + NaSO_3 3H_2O \tag{1}$$

$$2Ag_{(s)} + Na_2S \rightarrow Ag_2S_{(s)} + 2Na \tag{2}$$

The morphology and chemical composition of silver surface after electrochemical process were studied by scanning electron microscopy (SEM, Hitachi, SU 3500) and energy dispersive spectroscopy (EDS). The surface morphology, root-mean-square roughness (R_{rms}) average roughness (R_{ave}) were characterized by atomic force microscopy (AFM, Digital Instrument, Inc., Santa Barbara, CA) by using tapping mode equipped with a standard Si tip. The CIE LAB of the samples were measured using a Hunter Lab Color Quest XE spectrophotometer with illuminant D65 and 10° observer.

Fig. 1 Silver samples for electrochemical process.

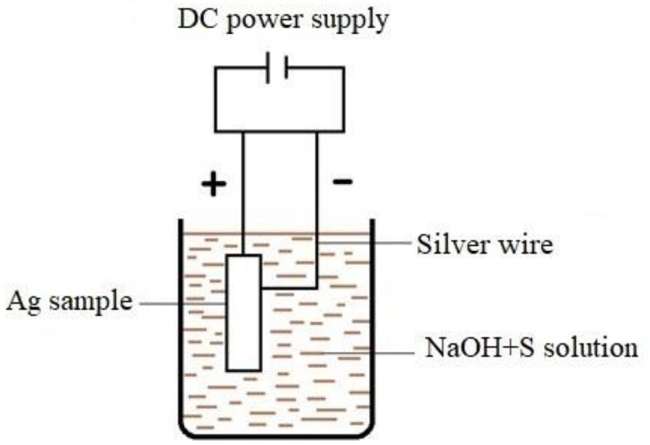

Fig. 2 Schematic diagram of electrochemical process.

Results and Discussion

Figure 3 and 4 show the SEM images of Ag_2S films on the silver surface when the applied voltage of 1.50 and 2 V was used for 30, 60, 90, 120, and 150 s. It can be seen that the morphology of Ag sample exhibited notable smooth surface and spherical structure. In addition, it can be seen that the density of particles tends to increase as the deposition time of immersion in electrolyte solution increases. The diameter of Ag_2S particles is in rang 0.50 – 0.60 micrometer, whereas that of Ag_2S particles are slightly larger, in rang 0.80 – 1 micrometer with increasing voltage from 1.50 – 2 V. Thus, the particle size of Ag_2S film was increased whereas the adhesion of film on the silver surface increased with increasing applied voltage. The silver sulphide was formed thin layer on the surface in solution because it contains two silver atoms, and silver is highly sensitive to sulfur than chloride, carbonate and nitrate [1].

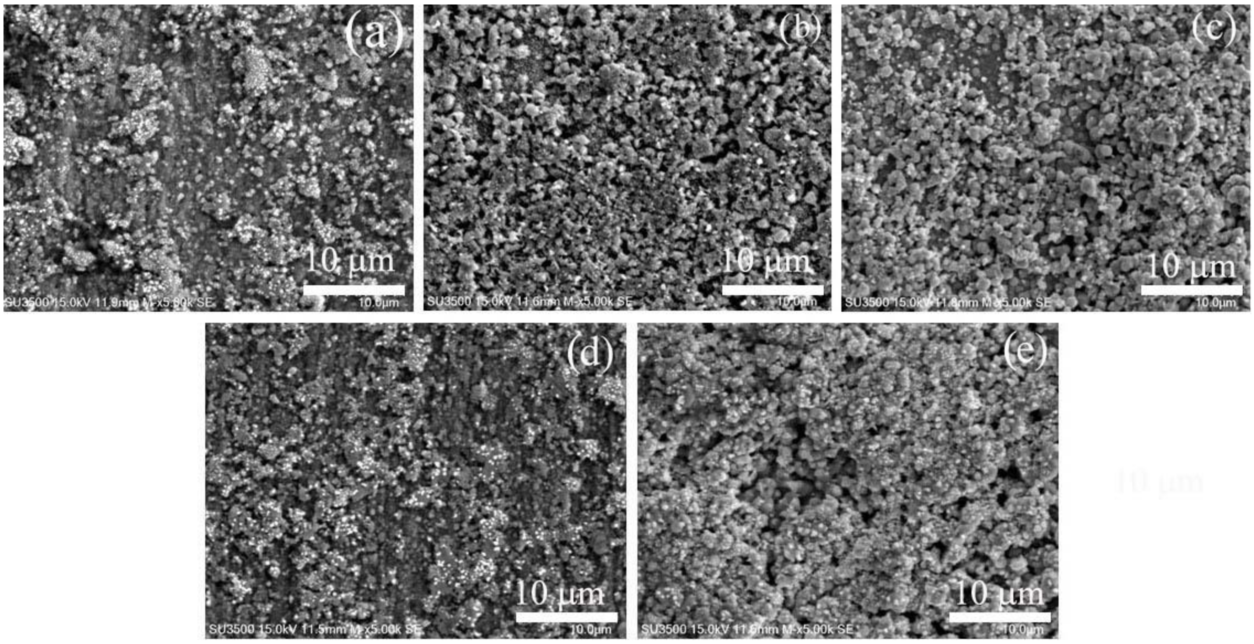

Fig. 3 SEM images of Ag_2S films form on the silver surface, applied voltage at 1.50 V for (a) 30, (b) 60, (c) 90, (d) 120, and (e) 150 s respective.

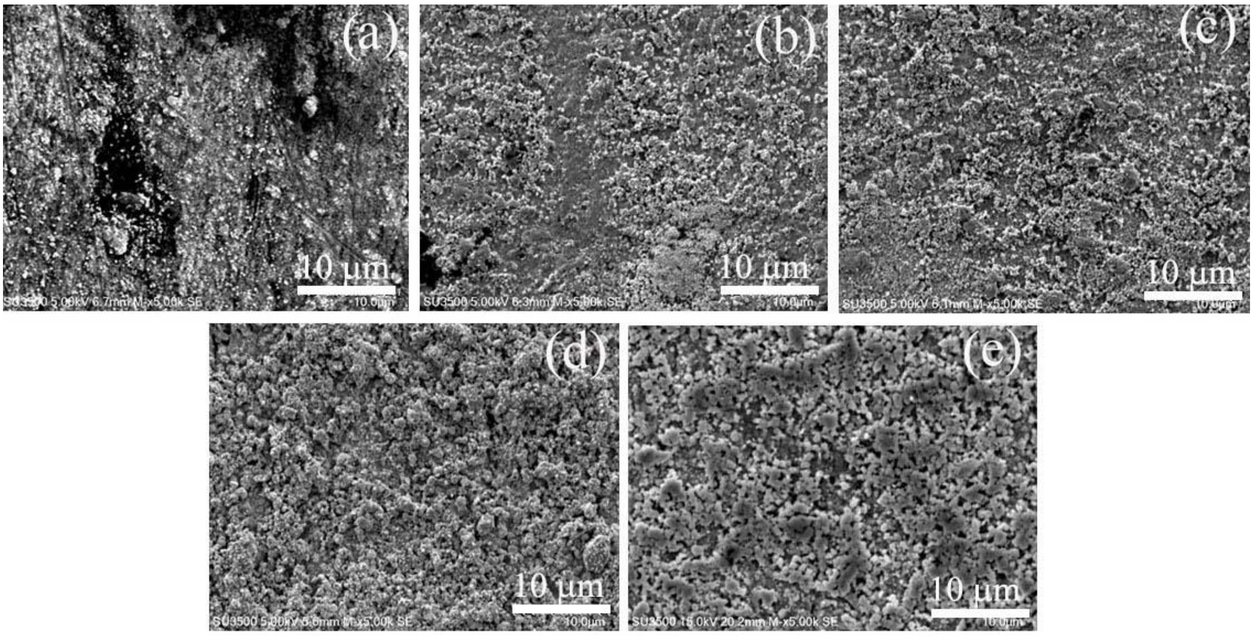

Fig. 4 SEM images of Ag_2S films form on the silver surface, applied voltage at 2 V for (a) 30, (b) 60, (c) 90, (d) 120, and (e) 150 s respective.

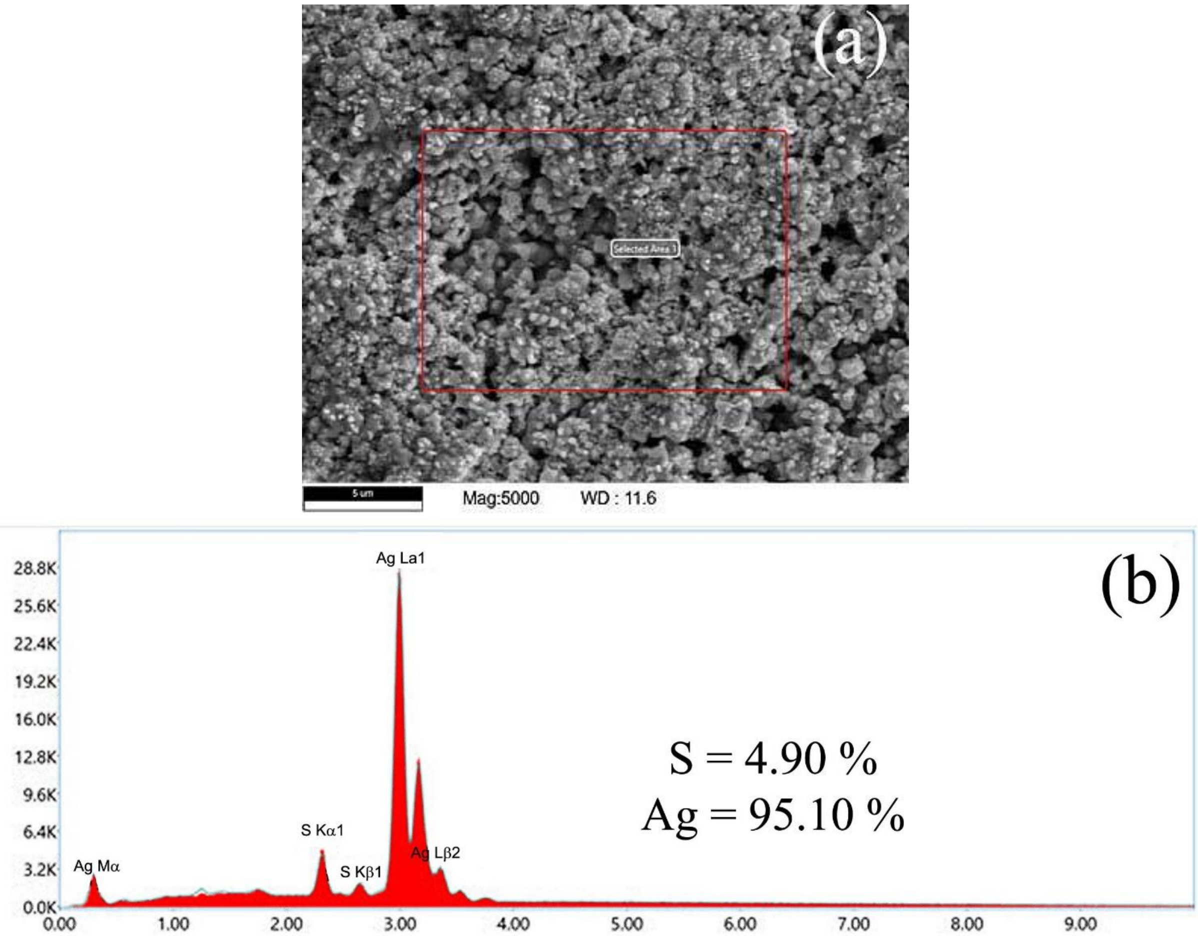

Fig. 5 EDX of Ag_2S film (a) EDX selected area and (b) spectrum peak of sulfur and silver.

The composition of Ag_2S film was determined by EDS analysis are shown in Fig. 5. The EDX results were analyzed using mapping mode as shown the spectrum of S and Ag. Silver sulfide formation was evident by color change from light-yellow-brown, for 30 s immersed sheets, to dark-yellow green for longer than 120 s immersions. This was also confirmed by EDS analysis where sulfur was detected at 4.90 wt.% and 95.10 wt.% on the silver surface after 150 s at deposition potential 1.50 V. Since the chemical composition of sulfur in this work is as high as about 3% which caused a relative immersion time and concentration of solution as compared to the previous reports [1, 6].

AFM images of the surface coating were shown in Fig. 6. It is obvious that voltage at 1.50 V (Fig. 6 (a), (b)) show the ripened and island-like domain structure of Ag_2S (Rrms = 40.289 nm, Rave = 29.099 nm) whereas applied voltage at 2 V (Fig.6 (c), (d)) was smoothened surface (Rrms = 25.063 nm, Rave = 17.927 nm). The Rrms and Rave roughness of films decreased with increase of the applied voltage in electrochemical process, this result indicated that the grain size of film was decreased. Furthermore, the grain sizes obtained from AFM images are slightly larger than those observed from SEM images, due to the broadening effect of the tip-shape convolution [7].

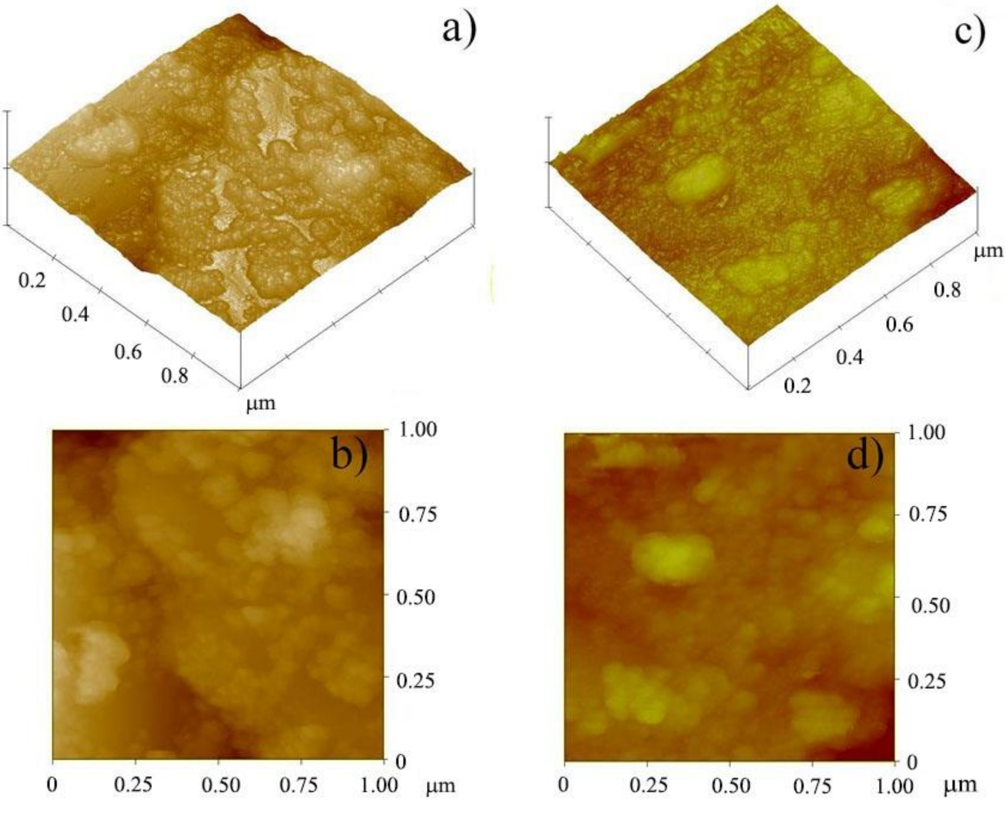

Fig. 6 AFM images of Ag_2S film form on silver surface, applied voltage at (a), (b) 1.50 V and (c), (d) 2 V for 150 s.

CIELab values of silver samples coating with Ag_2S are given in Table 1. The lightness (L*) values of the 2 V samples were higher than that of 1.50 V for all electrolyze time. From L*a*b* plot (Fig. 7), it can be seen that the colors of Ag_2S films were shifted from red-blue to yellow-green co-ordinate in CIELab color space. Moreover, a shift towards dark yellow-green was higher in case of the deposition potential at 2 V with increase of immersion time for 150 s. In the case of applied voltage below 1 V, the image shows in Fig. 8, the color of Ag_2S films could be changed from yellow through red, green, blue and yellow again Fig. 8 (a). The thickness of Ag_2S films on silver surface can be controlled by voltage value and time of immersed in a solution. Thus, in this research, we selected the condition with the applied voltage 1.50 V and immersion time of 150 s in the electrolyte solution for coating silver jewelry product shown in Fig. 9.

Table 1 CIE LAB of Ag_2S films.

Volt	Time (s)	L*	a*	b*
1.50	30	44.73	-0.92	-2.68
	60	40.87	-1.60	-2.49
	90	49.63	-1.44	-2.94
	120	35.59	-1.01	-1.43
	150	31.96	-1.10	-2.47
2	30	58.92	-1.30	-1.03
	60	53.20	-1.53	-2.88
	90	46.23	-0.55	-1.52
	120	38.33	-1.59	-2.26
	150	42.70	-1.89	-3.00

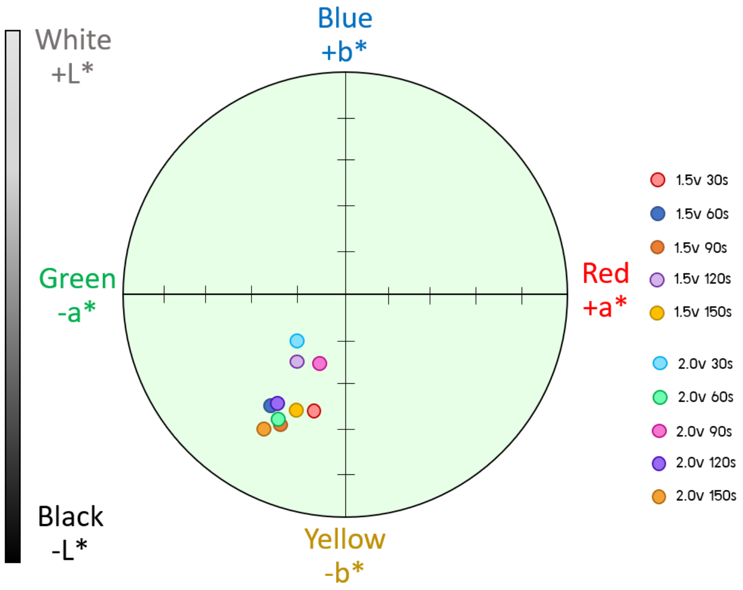

Fig. 7 L*a*b* plot of Ag_2S colors, applied voltage at 1.50 V, 2 V for 30 – 120 s.

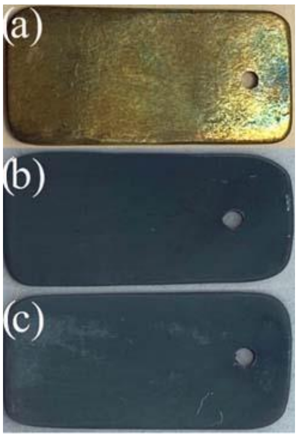

Fig. 8 Color of Ag_2S films on the silver surface, (a) 1 V, (b) 1.50 V and (c) 2 V for 150 s.

Fig. 9 Silver jewelry products coating with Ag_2S films, (a), (b) ring and (c) chain.

Conclusion

The electrochemical process for Ag_2S film preparation is very simple and low cost. The film quality such as color and smoothness of the silver jewelry product is as good as that of films prepared by painting and enameling method. The thickness and color of Ag_2S films can be controlled by varying the applied voltage and immersion time in the electrolyte solution. The creating color of patterns on silver jewelry is easily obtained.

Acknowledgement

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