JNPS 8 (3): 13-19 (2022)
ISSN: 2392-473X (Print), 2738-9537 (Online)

Research Article *© Nepal Physical Society*
DOI: https://doi.org/10.3126/jnphyssoc.v8i3.50717

Comparative Study of Fire-Gilded and Electroplated Gold Films on Copper Substrates

P. Joshi[1, *], N. Maharjan[2] and M. L. Nakarmi[2, **]
[1]Department of Physics, Bhaktapur Multiple Campus, Tribhuvan University, Bhaktapur, Nepal
[2]Department of Physics, Brooklyn College and the Graduate Center of the City University of New York, Brooklyn, New York 11210, USA
Corresponding Emails: [*]prakash.joshi@bkmc.tu.edu.np, [**]mlnakarmi@brooklyn.cuny.edu

Received: *16th June, 2022;* ***Revised:*** *7th Sep., 2022;* ***Accepted:*** *10th Dec., 2022*

ABSTRACT

We compared the structural and optical properties of the gold films deposited on copper substrates by the traditional fire-gilding method and electroplating method which are being adopted by the craftsmen in the Kathmandu valley, Nepal. Atomic force microscopy (AFM) and reflectance spectroscopy were employed to characterize the surface morphology and optical reflectance of the samples, respectively. In the AFM images of the surface of the gold films, we observed that the surfaces of the fire-gilded films not only are smoother but also have higher reflectance than that of the electroplated gold films. In the corrosion experiment by chemical etching of the gold films, fire-gilded samples showed superior corrosion resistance than electroplated gold films.

Keywords: Corrosion resistance, Electroplating, Fire-gilding, Gold thin film, Reflectance, Surface morphology.

1. INTRODUCTION

The Kathmandu valley, Nepal is rich in medieval era monuments. Fire-gilded copper-based objects such as roofs, pinnacles, gates, statues, etc. are essential parts of such monuments. Fire-gilding is a technique of coating thin films of gold (generally a few microns thick) onto a metal such as copper by applying the gold-amalgam paste on its surface first, and then evaporating the mercury with heat treatment [1-3]. The fire-gilded metal layer protects the gilded objects against their degradation in the ambient atmosphere for hundreds of years [1]. Additionally, it enhances the beauty and value of the gilded objects. Fire-gilding technique is a practically applicable method for coating gold thin films on large-sized objects [1] like pinnacles of temples, roofs, and windows of palaces of historic monuments. Nepalese craftsmen have been adopting this traditional technique of deposition of thin film of gold for several centuries [1]. However, the skyrocketing price of gold and hardship in purchasing mercury (required for preparing the gold amalgam) coupled with the possible health hazards of the craftsmen due to the toxic effect of mercury have motivated some of the craftsmen to adopt alternative methods like deep-coating and electroplating method for coating thin film of gold on metal these days. Electro-plating has been used to coat gold film mostly on small objects like ornaments and metal sculptures. Modern gold coating methods such as evaporation [4] and sputtering [4, 5] need high vacuum systems and they are generally very expensive. On the other hand, electroplating is considered low-cost and less health hazardous compared to the fire-gilding technique for gold deposition [6]. Though the electroplating technique is believed to be introduced in Nepal in 1979, this technique is not popular among the craftsmen compared to the traditional technique of gold deposition as they believe that the electroplated gold film (adopted by the craftsmen in the Kathmandu valley for commercial purpose) is less attractive and less stable compared to the fire-gilded film [6].

In our previous work on the characterization of fire-gilded gold film, we have explored the surface morphology, elemental analysis, and optical property of the fire-gilded films deposited on copper substrates [1]. In this paper, we present a comparative study of the surface morphology, optical reflectance, and corrosion resistance of the fire-gilded and electroplated gold films on copper substrates prepared by the craftsmen (in the Kathmandu valley) and we also discuss why the electroplated gold film is not as attractive as the fire-gilded film.

2. EXPERIMENTAL

2.1 Preparation of fire-gilded and electroplated gold film samples

Two types of samples--fire gilded and electroplated gold films on copper substrates-- were prepared by the local craftsmen in the Kathmandu valley for this study. The samples of fire-gilded film and electroplated gold film have been named FG and EP, respectively.

The method of the preparation of the fire-gilded samples was similar to that described in our previous work [1]. Photographs taken at various steps of the sample preparation in the fire-gilding method are shown in Figure 1. The preparation method of the fire-gilded sample is briefly described here. First, the gold-mercury amalgam was prepared by mixing minute pieces of gold flakes in mercury with gold to mercury ratio of 1:5 by weight. The mixture was then ground with glass powder in a stone mortar and pestle till all gold flakes were uniformly dissolved in the mercury. A photograph of typical stone mortar and pestle used in grinding is shown in Figure 1(a). The glass powder was added to facilitate the abrasion of the gold flakes. While grinding, the rim of the mortar was frequently rinsed with water. After several hours of grinding, the gold flakes completely dissolve in the mercury. The gold mercury amalgam accumulates at the bottom of the mortar. The water and glass powder in the mortar were then removed by soaking up it with a piece of cloth or sponge. Figure 1(b) shows a photograph of mercury amalgam placed in a plate.

Next, the copper substrates were cleaned first by heating them in the flame of a petroleum gas burner to burn dirt on them, and then immersing them in dilute sulfuric acid solution. The substrates were then cleaned with a piece of cloth or sponge. Just before coating the copper substrates with the gold-amalgam, surface was further cleaned by scrubbing with a soft brass brush and finally rinsed with water. A photograph of cleaned copper substrates is shown in Figure 1(C). The gold amalgam was then coated onto the cleaned copper substrates using a metal rod as shown in Figure 1(d). The surface looks white with the paste of gold amalgam. The copper substrate with the coated paste of gold amalgam was heated by flame of a gas burner to evaporate the excessive mercury as depicted in Figure 1(e). The fire-gilded surface then turned into yellow as shown in Figure 1(f). It is believed that mercury forms solid solution with gold during the heating process [7]. The gold film fused on the copper was then cleaned in an aqueous alkaline solution derived from Ritha (*Sapindusmukorossi*). Finally, the gold film was burnished to enhance the golden shining [1].

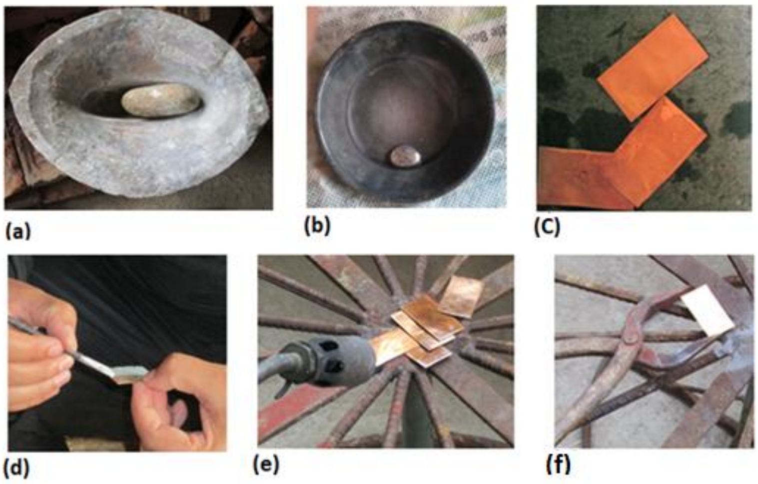

Fig. 1: Photographs showing steps of preparation of fire-gilded films: (a) typical stone mortar with pestle used for preparing gold amalgam, (b) gold amalgam in a plate, (c) clean copper substrates, (d) coating gold amalgam on a copper substrate with a metal rod, (e) heating the amalgam coated copper substrate in the flame of a gas burner, and (f) gold film on copper substrate after evaporation of mercury.

Similarly, the electroplated gold films on copper substrates were also prepared by craftsmen at their workshop in Patan, Nepal. The electroplating was carried out by using the cleaned copper substrate as one electrode and pure bulk gold as another electrode immersed in the potassium-based electrolyte.

2.2 Characterization

The surface morphology of the gold film samples was characterized by using a Digital Instrument atomic force microscopy (AFM). Images were taken in the tapping mode. Reflectance of the fire-gilded and the electroplated gold films was investigated using reflectance spectroscopy. In the reflectance experiments, the gold films under investigation were illuminated with the light from a tungsten-halogen lamp along with a monochromator (that has a grating of 1200 line/mm) at an angle of incident ~23º. This is the optimized angle for our experimental set up and detector. The intensity of the reflected light from the gold film was measured by using a silicon detector [1].

For a comparative study of the corrosion resistance of the gold films, the fire-gilded and electroplated gold film samples were immersed simultaneously in the solution of gold etchant for an equal duration of time. The gold etchant was prepared by dissolving ~ 0.2 g of Potassium Iodide (KI) and ~ 0.05 g of Iodide (I_2) into ~20 ml of distilled water. The AFM images of the gold films without and with treatment in the gold etchant were taken for their comparison. Similarly, optical reflectance of the etched gold films was also measured for comparison.

3. RESULTS AND DISCUSSIONS

3.1 Surface morphology of the gold films

We took images of (a) FG and (b) EP gold film samples using the AFM to compare the surface morphology. Figure 2 shows the AFM images scanned in 5 μm × 5 μm image size. Both top-view and 3D view images are shown for clarity. The surface morphology of the FG sample has feature of flat surface whereas the EP sample has more grain-like features on the surface. The z-height scale of the AFM image of the FG sample is 50.0 nm whereas it is 250.0 nm that of the EP sample. The rms values of the surface roughness of the FG and EP samples are about 8.1 nm and 21 nm, respectively. It clearly shows the surface of the FG sample is smoother compared to the EP sample.

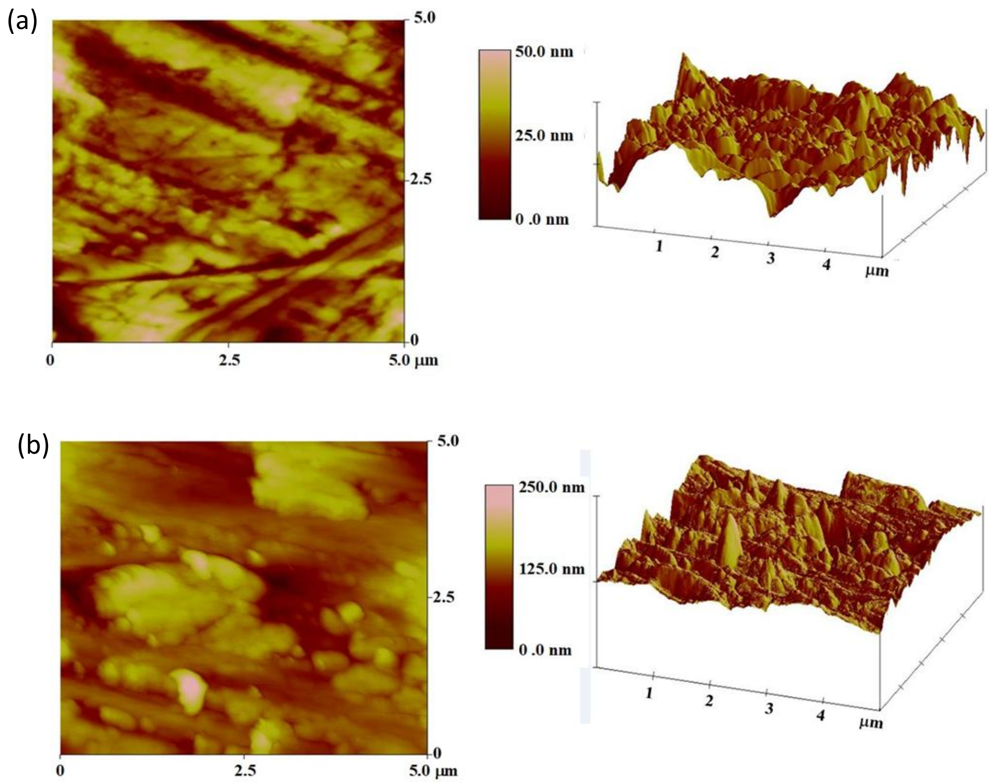

Fig. 2: AFM images showing 5 μm x 5 μm top view (left) and 3D view (right) of (a) FG gold and (b) EP gold samples.

3.2 Optical reflectance of the gold films

In order to compare the optical behavior of the fire-gilded and electroplated gold films, we measured the optical reflectance and compared the relative intensities. Figure 3 shows the relative reflectance of the gold films scanned in the visible spectral range of wavelengths from 400 to 700 nm.

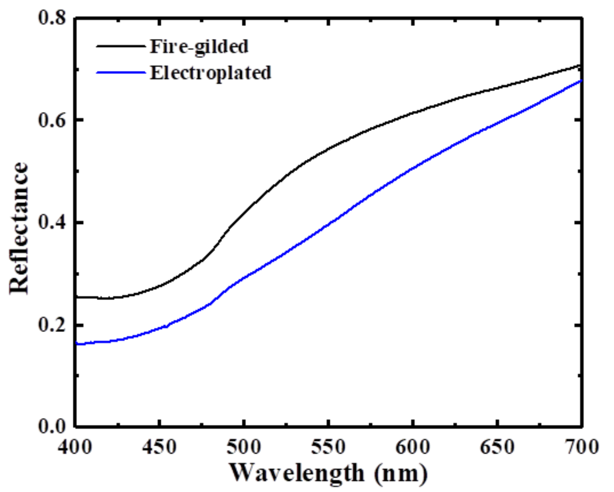

Fig. 3: Comparison of optical reflectance of fire-gilded and electroplated gold films.

From the reflectance spectra, we found that the reflectance of FG is higher compared to EP samples over the entire visible spectrum. This implies that the gold films deposited by the traditional method are more vivid than the electroplated gold film. The reflectance of bulk gold is about 0.4 in the UV region (λ > 300 nm) and it begins to increase from wavelength ~ 482 nm and becomes maximum in the IR region [8]. Bright yellow metallic luster of bulk gold is attributed to its sharp band edge at ~500 nm [9]. Higher reflectance of the FG compared to that of the EP sample correlates with the smoother surface of the FG surface in the AFM images shown in Figure 2. A smooth surface with high reflectance especially above 500 nm gives the golden luster on the gold surface making it attractive.

3.3 Corrosion resistance of fire-gilded and electroplated gold films

For a long life of the gold coated surface, it should have strong corrosion resistance. We investigated corrosion resistance of the gold films by immersing them in the gold etchant prepared with solution of Potassium Iodide and Iodide in water. Figure 4 shows the photographs of the gold films before and after etching and a copper substrate as a reference. Figure 4(a) and 4(b) are photographs of the FG sample before and after immersing into the gold etchant. Similarly, Figure 4(c) and 4(d) are photographs of the EP sample before and after immersing into the gold etchant. Both gold film samples were immersed into the etchant for ~5 minutes. Figure 4(b) clearly shows that the FG sample retains golden yellow luster whereas the EP sample lost yellowish shining of golden color as shown in Figure 4(d). In our observation, EP films start fading from ~2 minutes after immersing in the gold etchant whereas FG samples retain golden yellow luster even after immersing in the gold etchant for 30 minutes. This indicates that gold film in EP was completely corroded by the etchant whereas the FG shows a robust character against the etchant.

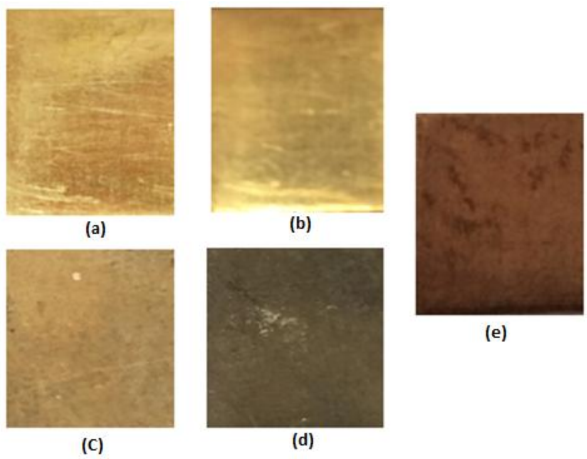

Fig. 4: Photographs showing (a) FG film before immersing in etchant, (b)FG film after immersed in etchant, (c) EP film before immersing in etchant, (d) EP film after immersed in etchant, and (e) copper substrate (C0).

In order to investigate the changes in microstructure on the surface of the gold films after immersing into the etchant, we performed AFM imaging of the samples. Figure 5 shows the AFM images of FG sample without and with treatment in the etchant, EP sample without and with treatment in the etchant, and a bare copper substrate (C0). Top view and 3D view images are shown for all three samples. Figure 5(a) is the AFM images of FG sample without treatment in the gold etchant and Figure 5(b) is after treated in the etchant. The shape of the grains seen in the Figure 5(b) was not different from that of the grains seen in Figure 5(a). This indicates that a significant amount of

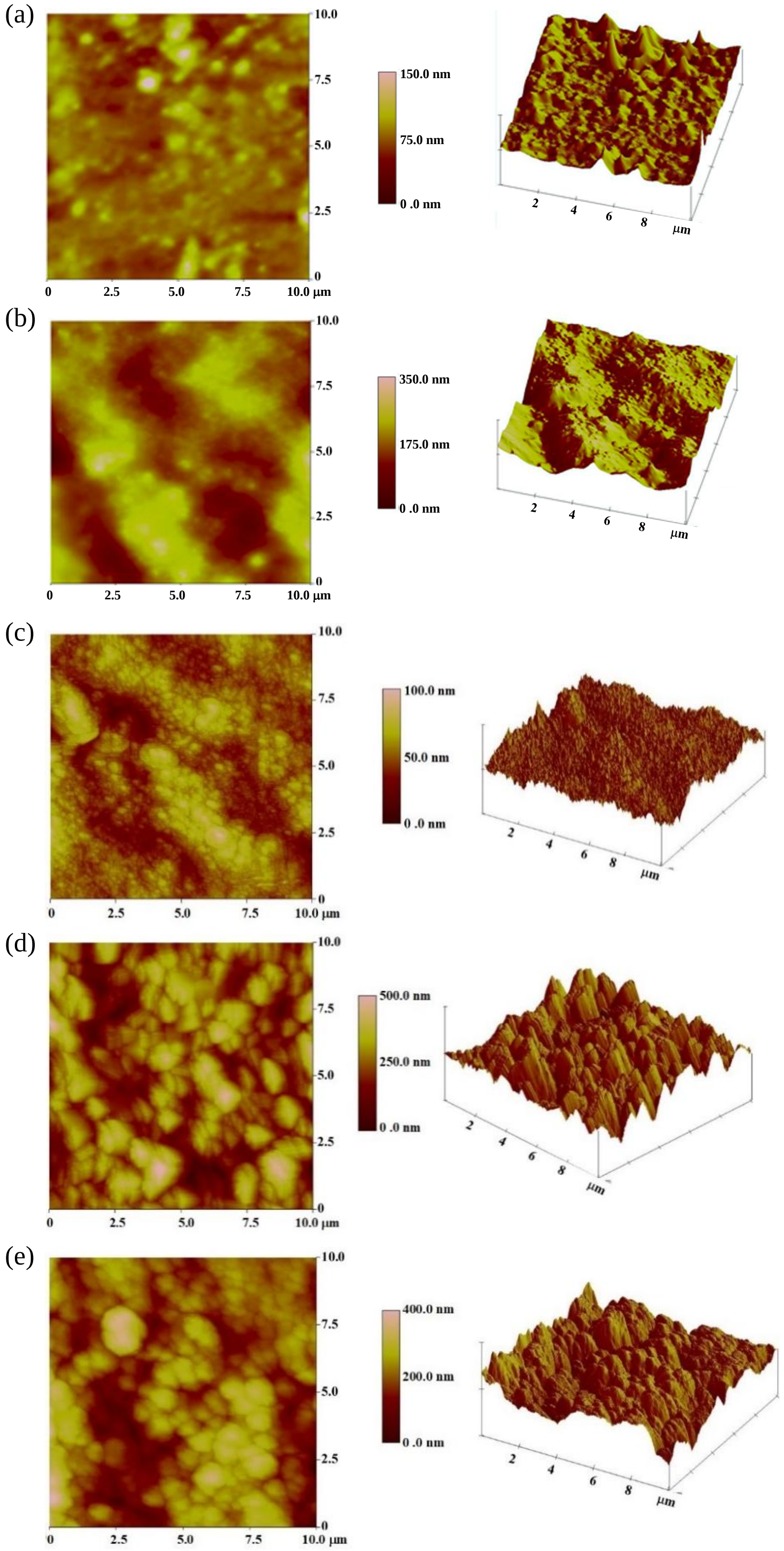

Fig. 5: Top view (left) and 3D view (right) of AFM images of (a) FG film, (b) FG treated with gold etchant (c) EP film, (d) EP treated with gold etchant and (e) copper substrate.

gold still exists after immersing FG into the gold etchant. Figure 5(c) is the AFM image of EP in which irregular shaped clusters of grains are visible. However, Figure 5(d) we got different observations in the case of the EP sample. The surface morphology of the etched EP is totally different from that of the electroplated gold film seen in Figure 5(c). Instead of the cluster of irregular shaped small grains, larger and round shaped grains are exposed. Figure 5(e) is an AFM image of a copper substrate, C0. Rounded grains with several hundred nanometers in dimension are distinctly seen in the image. The morphology of the EP sample treated in the gold etchant is, in fact, analogous to the morphology of C0 with irregular shaped grains. This indicates that the electroplated gold has been completely corroded by the gold etchant exposing the copper substrate. Additionally, the surface morphology of the substrate is also modified showing poor resistant of the electroplated gold film to corrosion. Results from the AFM imaging are consistent with the photographs of gold films after immersing into the gold etchant discussed above. Our observation clearly shows that the gold film deposited by the traditional method is more robust against corrosion compared to the electroplated gold film. It is believed that during the heating process to evaporate mercury in the fire-gilding method, solid-state reaction occurs with residual mercury and gold [7]. The gold amalgam formed in the solid-state reaction could bond the gold film strongly with the copper substrate at the interface of the FG films.

We also performed the optical reflectance measurements of the etched samples for comparison. Figure 6 shows the relative reflectance of the copper substrate (C0), etched electroplated gold film (etched EP), and etched fire-gilded film (etched FG). The reflectance of the etched FG is significantly higher than that of the etched EP and C0. In fact, the reflectance of etched EP is less than that of C0. The lower reflectance of the etched EP than C0 indicates that there is not only complete corrosion of the gold film of EP by the etchant but the etchant also corroded the copper substrate turning the substrate rougher than C0. On the other hand, the higher reflectance of the etched FG compared to the etched EP implies that significant amount of gold remained on the FG even after immersing the film into the gold etchant. The reflectance results obtained here are correlated with the AFM images and photographs of the samples as discussed above.

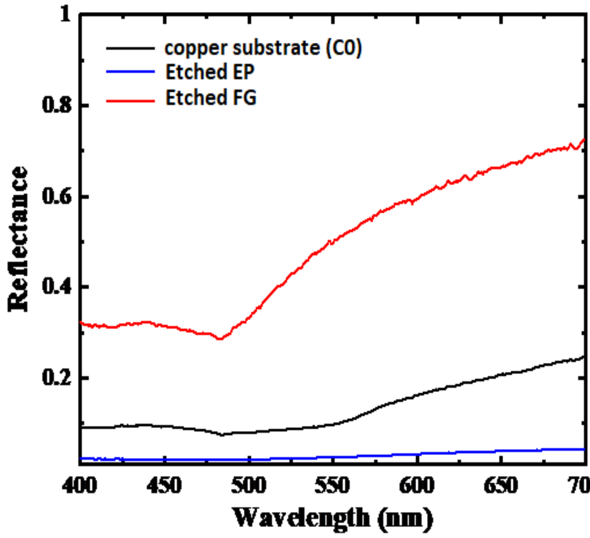

Fig. 6: Reflectance of copper substrate and etched gold films.

4. CONCLUSION

We compared the surface morphology, reflectance, and corrosion resistance of the gold films on copper substrates prepared by the fire-gilding and electroplating methods. The fire-gilded films have smoother surface morphology compared to that of the electroplated gold films. Higher reflectance of the gold surfaces correlates with the smoothness of surfaces. Thus, we found that the fire-gilded film exhibited superior reflectance compared to those of the electroplated gold film. Higher reflectance of the fire-gilded films rendered them bright yellow and more attractive than the electroplated gold films. Based on the corrosion experiment by chemical etching of the gold films, fire-gilded samples showed superior corrosion resistance than electroplated gold films. Existence of the gilded surfaces of the monuments and temple roofs manifests the robust corrosion resistance of the fire-gilded films.

ACKNOWLEDGMENTS

The authors acknowledge Mr. Jeevan Shakya, Goldsmith from Patan, Nepal, Mr. Rajan K.C., craftsman from Patan, Mr. Hem Krishna Tamrakar and Mr. Dwarika Tamrakar, coppersmith & craftsman from Patan, Mr. Suresh Man Lakhey, Officer at Patan Museum, Mr. Krishna Gopal Prajapati and members of Wakupati Narayan Temple renovation committee, Bhaktapur, Nepal, Associate Prof. Sudarshana Shakya, Assistant campus chief (Science and Technology) Bhaktapur Multiple Campus (BMC), T.U., Nepal, BMC, and

Dr. Anupam KC at Texas State University, San Marcos, USA.

REFERENCES

[1] Joshi, P.; Maharjan, N.; K.C., A. and Nakarmi, M. L. “Characterization of gold thin films deposited by centuries-old fire-gilding method,” *Indian Journal of Pure & Applied Physics*, **60**: 117–125 (2022).

[2] Shrestha, S. S. “Gold gliding (A traditional craft in Kathmandu Valley),” *Ancient Nepal*, **128-129**: 5-9 (1992).

[3] Singh, V. and Singh, S. “Mercury-amalgam gilding in Nepal: A study of traditional material and technique,” in Metal 2016: proceedings of the interim meeting of the ICOM-CC Metals Working Group, edited by M. Raghu, C. Claudia, and P. Achal (ICOM and IGNCA, New Delhi, 47–52 (2016).

[4] Martin, P. J. “Ion-enhanced adhesion of thin gold films,” *Gold Bull.* **19**: 102 (1986).

[5] Libansky, M.; Zima, J.; Barek, J.; Reznickova, A.; Svorcik, V. & Dejmkova, H. “Basic electrochemical properties of sputtered gold film electrodes,” *Electrochimica Acta*, **251**: 452 (2017).

[6] Furger, A. R. “The gilded Buddha: The traditional art of the Newar metal casters in Nepal,” (LIBRUM Publishers & Editors, Basel, Frankfurt a.M. (2017).

[7] Anheuser, K. “The practice and characterization of historic fire gilding techniques,” JOM **49**: 58–62 (1997).

[8] Stenzel, O.; Wilbrandt, S.; Stempfhuber, S.; Gäbler, D. and Wolleb, S. J. “Spectrophotometric characterization of thin copper and gold films prepared by electron beam evaporation: Thickness dependence of the drude damping parameter,” Coatings, **9:** 181 (2019).

[9] Blaber, M. G.; Ford, M. J. and Cortie, M. B. Gold: Science and Applications, edited by C. Corti and R. Holliday (CRC Press, Florida, 2010) Chap. *The Physics and Optical Properties of Gold*, 13–29 (2010).