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Characterization of Gold Thin Films Deposited by Centuries-old Fire-gilding Method

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We have explored the centuries-old fire-gilding method which is being practiced by craftsmen in Nepal. In this technique, gold films are deposited on metal by heating the paste of gold amalgam layer coated on the metal surface. Samples of gold thin films deposited on copper substrate by this traditional method were characterized by x-ray diffraction (XRD) for structural properties, and atomic force microscopy (AFM) and scanning electron microscopy (SEM) for surface morphology. The XRD pattern of the samples showed the formation of polycrystalline gold film on the copper substrate. Microstructure characterization of the surface morphologies from the AFM and SEM images showed the gold films have porous feature with submicron size pores. We also performed optical reflectance measurements of the gold films deposited by this method to investigate the effects of double coating of gold amalgam layers, burnishing process and iron oxide treatment on the gold film. We found that the optical reflectance is increased as the surface smoothness is increased by double coating and burnishing. We also found that the vivid golden luster is enhanced by iron oxide treatment due to increased reflectance in the red spectral region.

Keywords: Gold films, Fire-gilding method, Surface morphology, Reflectance

1 Introduction

Gold has been adopted as a precious and ornamental element by human being from ancient time. Generally, gold in bulk is used for making small ornaments. Thin gold film can also be seen on the surface of metal-based artifacts, handicrafts, roofs, statues, entrances of centuries-old temples, and monuments. The golden gate[1] at the mediaeval royal palace in Bhaktapur (Kathmandu valley, Nepal) constructed in 1754 is an example of a large size metal (copper)-based monument coated with a thin gold film. Generally, bare copper turns into unattractive greenish color due to oxidation when it is exposed to moist air in ambient environment. Coating the metal surface of such monument with a layer of gold increases its glory and preserves it from atmospheric corrosion for a long period even over several centuries. Existence of centuries-old, gilded monuments like the golden gate mentioned above indicates that there exists a traditional technology of depositing thin gold film on metal surface in the mediaeval Nepal.

These days thin gold film can be deposited by various methods like evaporation[2], sputtering[2,3], and electroplating[4,5]. These techniques are inconvenient to deposit gold on large sized objects like roofs of temples on sight. Several different techniques have been used for gilding metal surface such as foil-gilding, leaf-gilding, diffusion-gilding and fire-gilding[6]. Here, we have explored the fire-gilding technique of depositing gold film on metal surfaces that has been adopted by the craftsmen in Nepal for centuries. This technique is also practical and the conventional method to coat gold film on big objects.

The centuries-old fire-gilding method of depositing gold film is carried out mainly in three steps: coating the paste of gold and mercury (gold amalgam) onto a metal substrate cleaned prior with an acidic solution; evaporating the mercury from the amalgam with heat treatment leaving a thin film of gold on the metal surface; and burnishing the gilded surface[7,8]. The thin gold film deposited by this method is not only simple and cost-effective, but also have excellent resistant against the atmospheric corrosion as evident by the still shining golden roofs and pinnacles of centuries-old temples in Nepal despite their continued exposure in the atmosphere. In spite of these salient features of this technology of depositing thin gold film, the scientific study on this technology of thin film deposition is still lagging and there exists a need to

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study the traditional method aiming to explore the physics of the gold film deposition which will also help preserve ancient heritages. Shrestha[7] & Furger[8] have disclosed various aspects of the traditional method of gold plating being practiced in Nepal. Similarly, Singh *et al.*[9] reported their investigation on atmospheric corrosion of a centuries-old gold-gilded window at the Patan Royal Palace in the Kathmandu valley, Nepal. Anheuser[10] studied the effect of temperature on fire-gilding techniques and he found that the gilding process is in fact carried out at low temperature and is a solid-state reaction that does not involve melting of the gold amalgam.

In this paper, we have studied the centuries-old fire-gilding method of depositing gold thin films by directly visiting craftsmen. We have characterized the gold thin film samples prepared by the fire-gilding method using atomic force microscopy (AFM) and scanning electron microscopy (SEM) for surface morphology, x-ray diffraction (XRD) for crystallinity, energy dispersive x-ray spectroscopy (EDS) in the SEM for chemical composition analysis and reflectance spectroscopy for optical properties. We studied the effects of double coating, burnishing process and iron oxide treatment on the surface smoothness and reflectance of the gold films.

2 Experimental

2.1 Sample preparation

The samples of gold thin films deposited on copper substrates were prepared by craftsmen in their workshops in Kathmandu valley, Nepal. The gold film deposition method was similar to the ones described elsewhere[7-8]. First, a thin sheet of gold was cut into flakes using a scissor. Then, mercury was added to the gold flakes in a ratio of the gold to mercury about 1:4 - 1:5 by weight. The mixture of the gold and mercury was kept in a stone mortar and small pieces of sharp-edged glass from broken tube of fluorescent lamp were added to the mixture. The mixture of the glass and the gold amalgam was ground with a stone pestle and rinsed regularly with water while grinding the amalgam. The powdered glass was removed by soaking up the water used to rinse the mixture using a piece of sponge. The grinding process continued for several hours until the gold completely dissolved into the mercury forming a homogenous paste of gold amalgam. Prior to the gold deposition, copper substrates were cleaned by heating on the flame of petroleum gas burner to burn dirt, then cleaned with dilute aqueous solution of sulfuric acid and rinsed with water to remove impurities adhered on the metal surface. The paste (gold amalgam) was then coated onto the freshly cleaned copper substrates using a small metal rod. The metal surface coated with the amalgam was then heated in the flame of gas burner for only few seconds and wiped the heated surface with a piece of cotton. When the surface temperature was measured right after firing was done at a spot using a Fluke 561 Infrared Thermometer, we obtained the temperature around 260 ^{o}C. Since the spot is heated just for few seconds, the real temperature could be higher than this as the heat can be dissipated quickly on these metals. This heating process was repeated until the silver white color of the amalgam coated onto the copper surface turned into brass yellow color assuring complete evaporation of the excessive mercury and fusion of a thin gold film on the copper surface. In the burnishing process to shine the gold surface with metallic luster, it was first washed with an aqueous soapy solution based on *Reetha* (*sapindus mukrossi*) and scrubbed with a soft brush, and then the surface of the cleaned film was rubbed with a polishing tool. The gold film was washed again with the soap water and scrubbed with a soft brass brush. Finally, the samples of gold films on copper substrates were rinsed with water and then dried.

Several samples of gold films were prepared for characterization, and to investigate the effect of burnishing. To characterize the gold films for structural property and surface morphology, two different gold film samples - one with single coating (named CT1) and another with double coating (named CT2), were prepared by the craftsmen using the traditional method. In order to investigate the effect of burnishing on the properties of the gold film, samples of gold film with and without burnishing were also prepared and collected from the craftsmen.

Even after burnishing the gold film, the gilded surface lacks the vivid golden yellow luster. The final step of brightening process is iron oxide treatment. In the iron oxide treatment, the paste of iron oxide prepared in water was coated onto the burnished gold film. After drying the iron oxide paste in sunlight, the gilded surface was heated shortly on a gas burner and the sample was immediately immersed into the soapy water based on *Reetha*. The surface of the sample was then scrubbed with a soft brass brush or *Pote* (glass beads used to make traditional necklace, typically used by Nepalese women) and rinsed with water. In

order to explore the effect of iron oxide treatment, two additional gold film samples – with and without iron oxide treatment were also prepared by the craftsmen.

2.2 Characterization

X-ray diffraction measurement was carried out using a Bruker D2 Phaser diffractometer with characteristic Cu K_α radiation of wavelength, λ = 1.54060Å. The surface morphology of the gold films was characterized by taking AFM images of the films using a Digital Instrument AFM in tapping mode. Similarly, the imaging of the samples was also performed by using Helios Nano lab 400 SEM. We also used the EDS mode in the SEM for chemical composition analysis. The optical reflectance of the gold film samples was measured by reflectance spectroscopy using a tungsten halogen light source, a monochromator with a grating ruled as 1200 line/mm and a silicon detector. The reflectance measurements were performed at room temperature with angle of incidence at about 23º. Reflected signal in the detector was collected via a lock-in amplifier using a chopper in the incident beam at the frequency of 100 Hz.

3 Results and discussions

3.1 XRD of the gold film

The XRD pattern of the gold film sample (CT1) deposited on copper substrate using the traditional method is shown in Fig. 1. The peaks observed at the values of 2θ at ~38.30º, 44.60º, 64.76º, and 77.45º are attributed to the diffraction of x-rays from (111), (200), (220), and (311) planes of gold, respectively[11]. Similarly, the diffraction peaks at ~ 43.19º, 50.24º, and 74.10º are due to (111), (200), and (220) planes of copper substrate, respectively[12]. These peaks confirm the formation of polycrystalline gold film on the copper substrate. Dominant XRD peak is from (111) plane in correlation with the copper substrate. Epitaxial layer is not expected as evident by the broad XRD peaks.

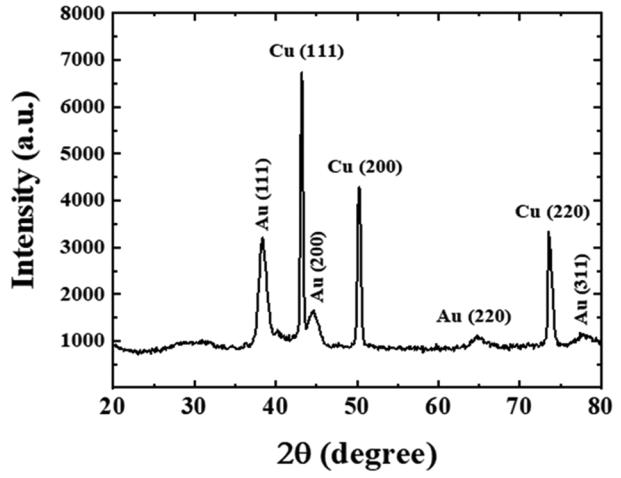

Fig. 1 — XRD of the gold film (CT1) deposited on copper substrate by traditional method.

3.2 Surface morphology of the gold films

We took AFM and SEM images for microstructure characterization of the surfaces of the gold films. Visually the surfaces of the gold films deposited by the traditional method look smooth with shiny golden color. Representative AFM images of the gold film with single coating (CT1 sample) with various magnifications are shown in Fig. 2(a-d) in the order of increasing magnification (*i.e.*, decreasing scanning area). These images depict several characteristics of the gold film deposited by the traditional method. The AFM image in the scan area (20 μm x 20 μm) in Fig. 2(a) shows that the surface has mostly smooth region with some micron-sized uneven gaps forming porous feature. A long and micron-sized wide pore is zoomed in Fig. 2(b). Some of such pores extend up to several microns longitudinally on the gilded surface. Fig. 2(c) shows the AFM image in a small scan area (2 μm x 2μm) in the smooth region. The images show that the smooth region of the gold film, in fact, consists of interconnected gold particles of different sizes in the order of few hundred nanometers. As shown in the AFM image with further zoom in Fig. 2(d), most of the gold particles are elongated (oval-shaped) and the boundaries between gold particles were seen distinctly.

For additional surface characterization and chemical composition analysis of the gold films, we performed imaging by SEM and EDS measurements, respectively. SEM image of a single coated gold film on a copper substrate is shown in Fig. 3(a). It also shows distinct porous feature on the gilded surface with gold particles in the order of few hundred nanometers size. These features of the gold film on SEM images are similar to the AFM images shown in Fig. 2. A magnified image is taken in the porous region to see the detailed microstructure and shown in Fig. 3(b). Fused gold particles along with submicron size pores can be clearly seen in the image. We also took cross section images of a single coated sample to estimate the thickness of the gold film as shown in Fig. 3(c). The thickness of the gold film on the single coated gold film is estimated to be about 2 μm

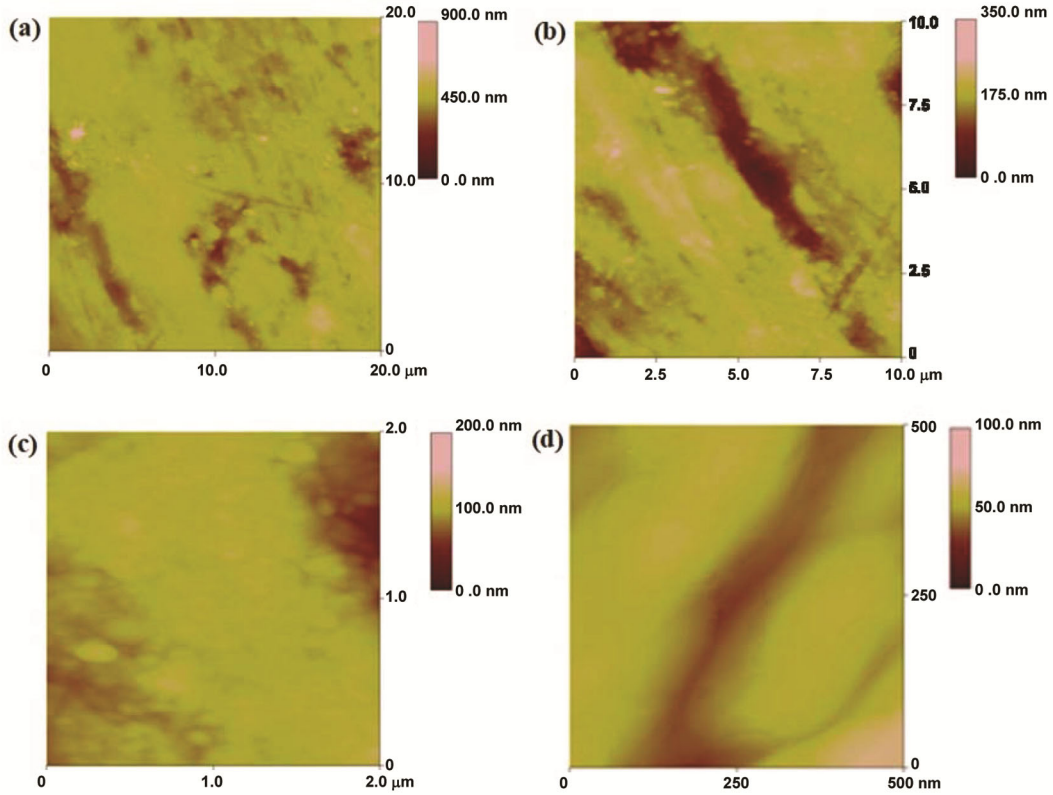

Fig. 2(a-d) — AFM images of gold film with single coating (CT1).

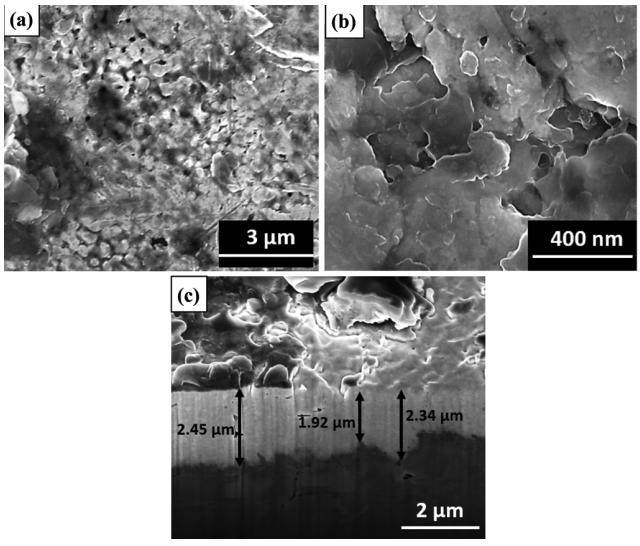

Fig. 3 − SEM images of gold film with a single coating (a) low magnification (~10 K) (b) high magnification (~65 K) and (c) cross section image.

although there is variation in the thickness as the paste of gold amalgam is coated manually.

During the fire-gilding process the samples are heated by the flame of gas burner for only few seconds. Repeating the firing process several times is a sintering process for complete evaporation of the metallic mercury and coalescence of gold particles on the substrate. We have attributed the porous feature with micron size gaps on the gold film to the evaporation of the excessive mercury. Anheuser[10] found that the fire-gilding process is a solid state reaction in which metallic mercury is first evaporated and then it further loses mercury from the amalgam. We believe the porous feature of submicron scale which is clearly observed in the SEM image could be due to the further evaporation of mercury from the alloy of the gold and mercury.

In order to explore the chemical composition in the gold film samples, EDS measurements were performed at several points in the smooth and porous regions in the SEM image. A typical EDS scan at the smooth region is shown in Fig. 4(a). The elements and their average percentages by weight are Au (72.4%), C (5.6%), O (3.7%), Cu (3.7%), Al (7.0%), Si (0.9%), and Hg (6.7%). Figure 4(b) shows a typical EDS scan at the porous region. The average percentages of elements by weight are Au (57.3%), C (9.5%), O (10.2%), Cu (9.7%), Al (4.5%), Si (3.2%), and Hg (5.5%). Obviously, gold (Au) is the dominant element in both regions. Observation of gold as dominant element in the porous region indicates the pores are

not extended up to the copper substrate rather there exist underlying gold particles inside the pore and such feature at the pore can also be seen in Fig. 3(b). A small percentage of mercury (~ 5 – 7% by weight) is present in the gold film which shows evaporation of mercury and the presence of metallic mercury is less likely. Detection of mercury in the gold is a characteristic of fire-gilding [6]. Mercury content in the range of 8 – 25% is possible in the fire-gilded films depending on the sintering conditions[10]. From our EDS results, the ratio of mercury to gold by weight is about 0.1 in both smooth and porous regions. Thus, we believe the mercury is forming solid solution with gold[10]. Carbon and oxygen are major impurities that could be from the contamination during sintering. Another residual impurity detected is silicon which might be from the glass and the sand of the stone mortar used to prepare the paste of gold amalgam that could also have contributed to the oxygen content. Copper signal is from the substrate. Signal from aluminum could also be generated from the substrate which is confirmed by EDS measurement of the copper substrate alone. The EDS of copper substrate is shown in Fig. 4(c). There is more EDS signal from copper substrate in the porous region. Furthermore, there are also more impurities such as C, O and Si in the porous region which could be due to more contamination in the porous region because of the difficulty in scrubbing these regions.

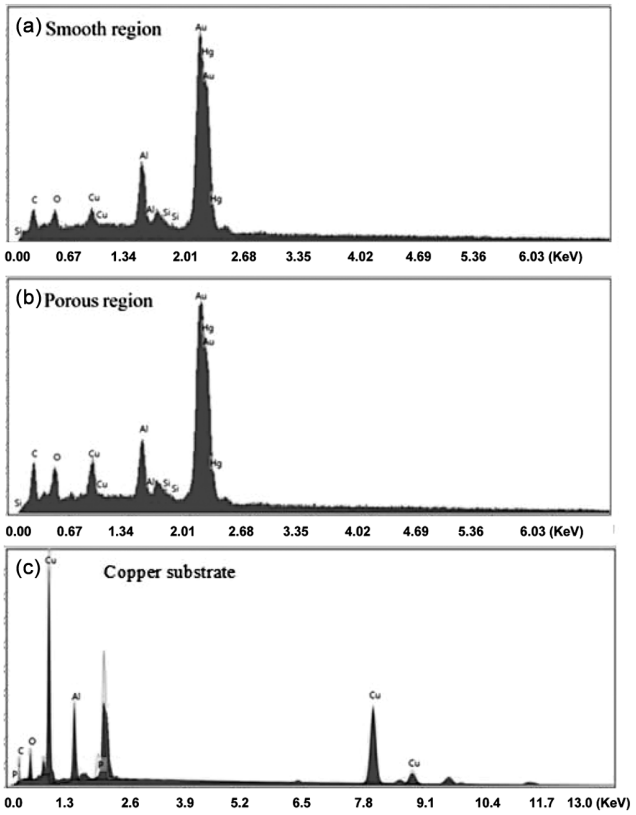

Fig. 4 — Typical EDS measurements of gold films at (a) smooth, (b) porous region and (c) copper substrate.

Figure 5 shows the AFM images of a double coated gold film sample (CT2) on copper substrate in different scan sizes. In the double coating sample, the second layer of gold amalgam was coated on a CT1 sample before burnishing and then the firing process was repeated. After that the surface was burnished. The AFM image shows that the oval shaped gold particles are found to be denser in the CT2 sample compared with those seen on the CT1. Though the uneven surface with variation of thickness on gold film is still noticed on CT2, the numbers of pores were less compared to those on the surface of CT1. Consequently, the surface roughness of the gold film on CT2 was found to be less compared to that of CT1. The root mean square (rms) value of the surface roughness on CT2 was ~ 24 nm, which is comparatively lower than that on sample CT1 which is ~34 nm. This shows that the gold particles on the

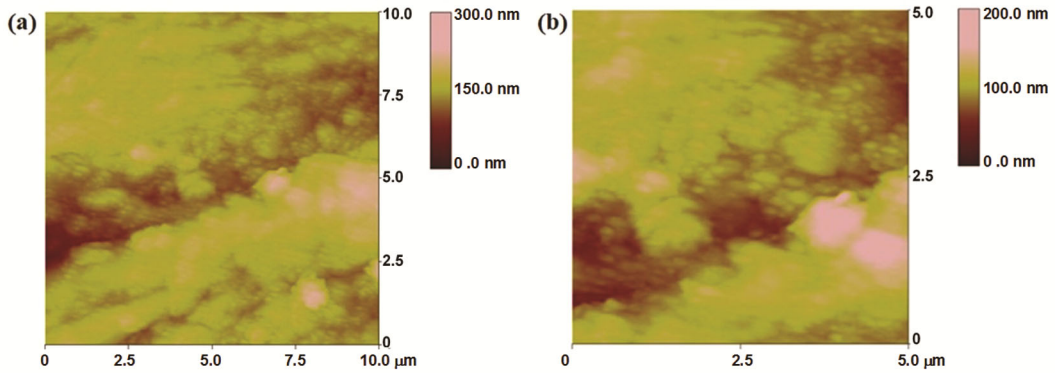

Fig. 5 — AFM images of the gold film with double coating (CT2 sample).

surface of the gold film with two coatings were found to be more homogenously distributed on the metal surface compared to the sample surface with single coating of gold film.

3.3 Optical reflectance of the gold films

We employed optical reflectance spectroscopy on the gold films to compare the reflectance of the single coat (CT1), and double coat (CT2) samples. Fig. 6 shows the relative reflectance of the gold films scanned in the visible range from 400 to 700 nm at room temperature. The optical reflectance of gold film for various wavelengths of incident light determines the brightness and color of the film. Gold efficiently absorbs wavelength ranging from violet to green and highly reflects from yellow to red colors in the visible light spectrum. Bright yellow metallic luster of bulk gold is attributed to its sharp band edge at ~ 2.4 eV (~500 nm)[13]. Reflectance of bulk gold is about 0.4 in UV region ($\lambda > 300$ nm) and it begins to increase from wavelength ~ 482 nm and becomes maximum in IR region[14]. Fig. 6 shows that the reflectance of CT1 and CT2 is smaller for violet to green color region, and then it increases up to the end of the visible spectrum. The relative reflectance of CT2 is higher than that of CT1 in the whole visible spectrum showing that the reflectance of the traditionally deposited gold film increases by adding second coating. The increase in reflectance of the gold film after double coating is attributed to the decrease in surface roughness of the latter film as evident from the AFM images. Relative reflectance of the CT2 compared to CT1 increases significantly in the wavelengths beyond ~ 500 nm up to red spectrum region. This implies that the double coating film is also more vivid than the single coated one. Generally, gold film having shine is more attractive.

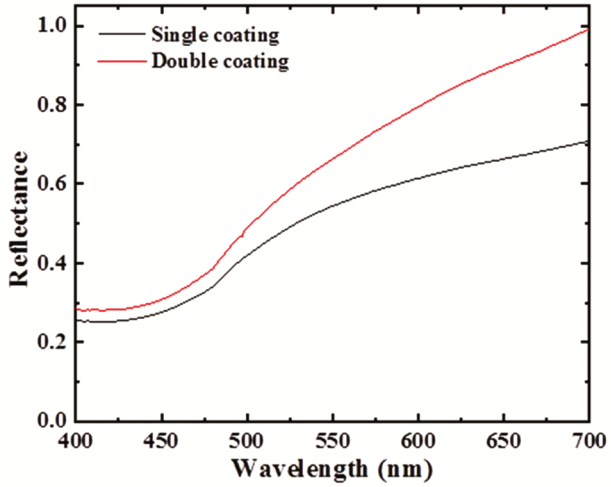

Fig. 6 — Reflectance of single coating (CT1), and double coating (CT2) gold films.

3.4 Effect of burnishing on the gold film

We have investigated the effect of burnishing on the surface morphology and optical reflectance of the gold films. We compared the AFM images of unburnished and burnished gold films which are shown in Fig. 7. Three-dimensional surface

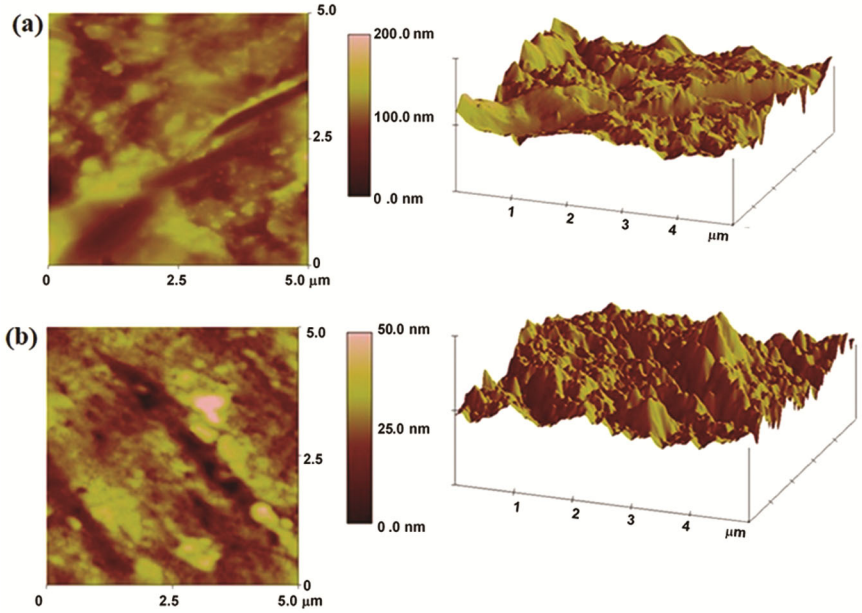

Fig. 7 — AFM images of gold films a) unburnished and b) burnished.

morphologies are also shown on the right sides to the top view images for clarity. The AFM images show that the surface of the burnished gold film Fig. 7(b) is significantly smoother compared to that of the unburnished gold film Fig. 7(a). The z-height scale in Fig. 7(a) for unburnished sample is 200 nm whereas it is 50 nm in Fig. 7(b) for burnished sample. Surface roughness is also improved from the rms value of about 20.3 nm in the unburnished sample to about 6.6 nm in the burnished sample.

We also compared the reflectance of the burnished and unburnished samples. Fig. 8 shows the relative reflectance of the burnished and unburnished gold films measured at room temperature. The reflectance of the burnished gold film is more than double compared to that of unburnished gold film. Gold is a malleable metal. During the burnishing process, when the gold surface is rubbed with a polishing tool, it helps smooth the surface. Generally, a smooth gold film is expected to appear brighter compared to a rough gold film. This argument agrees with the reflectance measurements of these two samples.

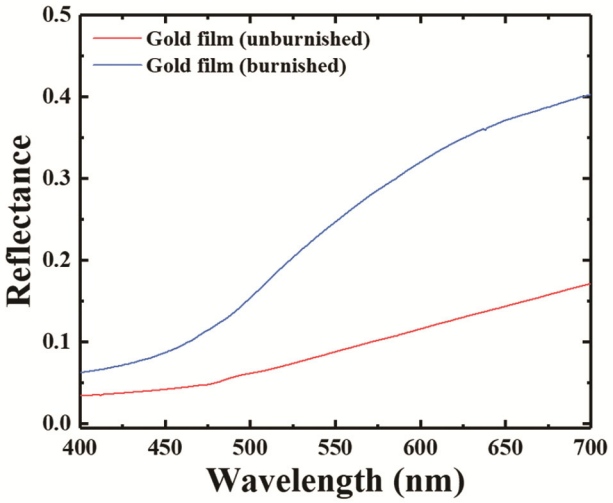

Fig. 8 — Relative reflectance of gold films with burnished and unburnished.

3.5 Effect of iron oxide treatment on the gold film

We have compared the surface morphology and reflectance of the gold film samples without and with iron oxide treatment. These samples were prepared with the gold to mercury ratio of 1:4 by weight. We also performed EDS measurements to explore the changes in the chemical composition in the gold films after iron oxide treatment. Fig. 9 shows the AFM images of the gold films (a) without and (b) with iron oxide treatment. Both top view and three-dimensional view are shown. The AFM images show the gold film treated with iron oxide Fig. 9(b) is smoother compared to the one without iron oxide treatment. The z-height scale of Fig. 9(a) is 300 nm whereas it is 75 nm in Fig. 7(b) for the samples without and with iron oxide treatment, respectively. The rms value of the surface roughness from the AFM image is about 30 nm on the sample without iron oxide treatment whereas it is about 11 nm on the sample showing significantly smother surface with iron oxide

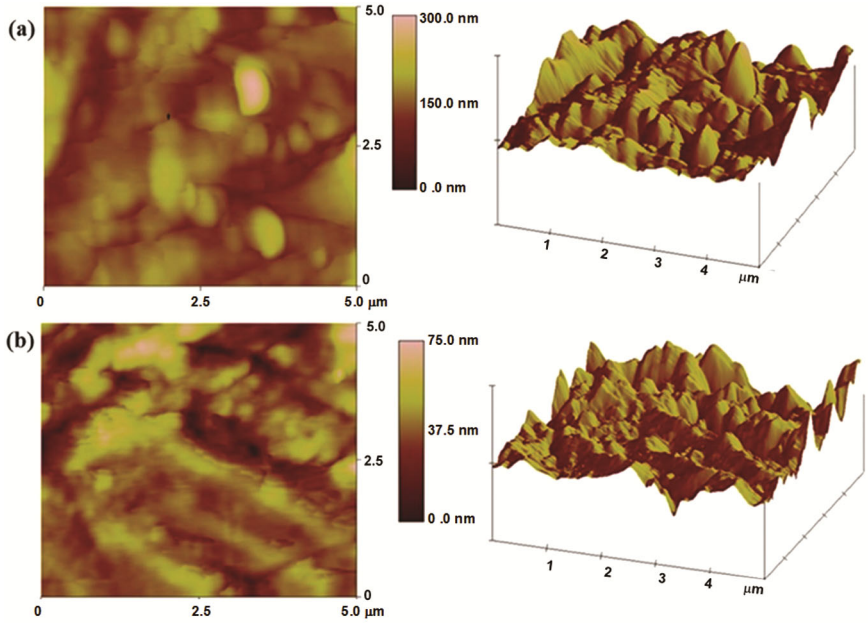

Fig. 9 — AFM images of gold film (a) without and (b) with iron oxide treatment.

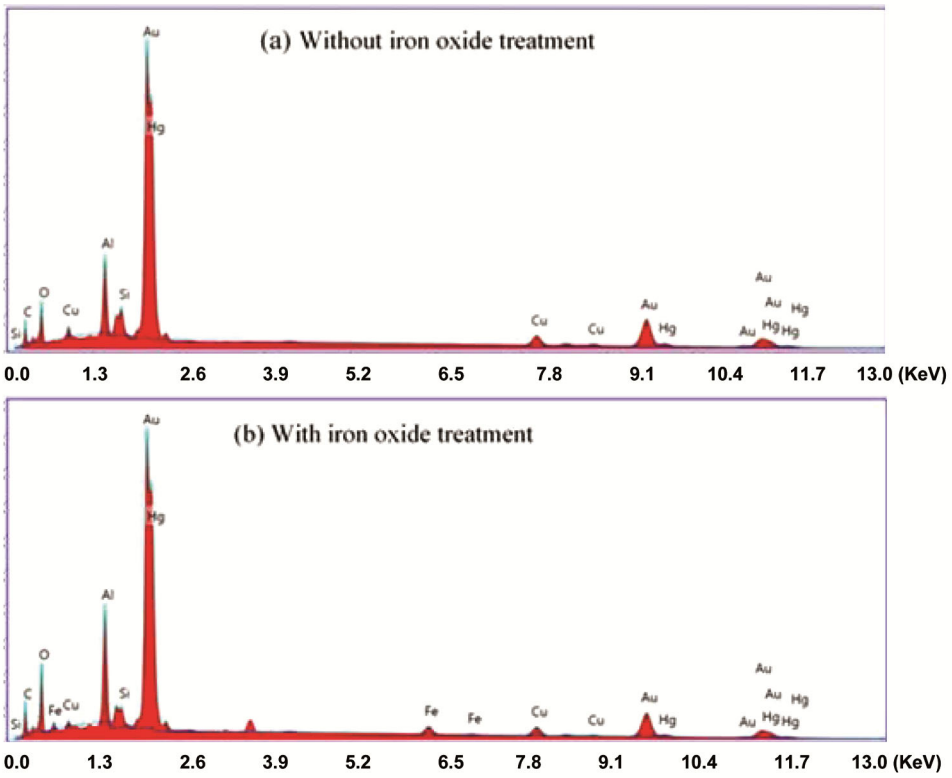

Fig. 10 — EDS results of gold film (a) without (b) with iron oxide treatment.

treatment. We believe the iron oxide fills the porous region making the surface smoother.

The EDS measurements of the gold films without and with the treatment of iron oxide are shown in Fig. 10. The prominent peaks seen in the EDS of the gold film treated without iron oxide Fig. 10(a) indicate the elements present (in percentage by weight) are Au (65.6%), C (7.9%), O (8.1%), Cu (3.6%), Al (5.6%), Si (1.6%) and Hg (7.5%). Similarly, the EDS of the gold film treated with iron oxide Fig. 10(b) indicates major elements present in the film are Au (57.7%), C (10.2%), O (12.1%), Cu (3.2%), Al (8.1%), Si (0.9%), Hg (5.8%) and Fe (2.0%). The detection of additional element, iron (Fe), and elevated value of oxygen in the iron oxide treated gold film confirms the adherence of the iron oxide on the gold film. The ratio of mercury to gold is about 0.1 which is same as in Fig. 4.

Figure 11 compares the relative reflectance of the gold films treated with and without iron oxide. It clearly shows that the reflectance of gold film treated with iron oxide increases significantly beyond ~500 nm and it is highest in the red color region. The gold treated by iron oxide gets the vivid golden luster which is normally done in gold jewelry to make it attractive.

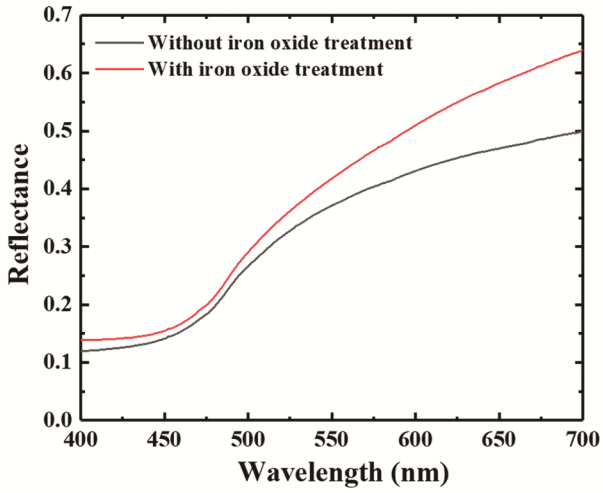

Fig. 11 — Reflectance of gold film without and with iron oxide treatment.

Based on the EDS result it is evident that iron oxide has been adhered on the gold film. Presence of iron oxide has contributed enhanced reflectance in red color region due to its intrinsic color. Thus, it clearly shows the vivid golden luster is enhanced due to the higher reflectance in the red spectrum region in the gold film with iron oxide treatment.

4 Conclusions

We have explored the centuries-old fire-gilding technology of depositing gold film on metal which is being adopted by the craftsmen in Nepal. The traditional method of gold film deposition is simple to adopt and practical to gild on large and on-site objects. We have characterized the surface morphology of the gold films on copper substrates prepared by the fire-gilding method using AFM and SEM, and found that the fire-gilded gold films have submicron size porous feature. The surface smoothness and the optical reflectance of the gold film can be increased by making double coating. Burnishing process increases the surface smoothness and reflectance enhancing brightness on the surface. Iron oxide treatment on the fire-gilded gold surface gives enhanced shining and enriched golden yellow luster due to the increased reflectance in the red region of the visible spectrum.

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