

Fabrication and Characterization of Reflectors by Physical Vapour Deposition of Nanoscale Thin Films of Ag and Cu for Concentrated Solar Thermal Power Applications

Christian N. Nwosu, Michael U. Onuu*

Department of Physics/Geology/Geophysics, Faculty of Science, Federal University, Ndufu-Alike, Ikwo, Nigeria

Abstract The Ag and Cu thin films were deposited using physical vapour deposition (PVD) technique which is a novel surface engineering method. Ag thin film of 100nm was deposited by thermal evaporation onto a thin microscopic glass substrate while the Cu thin film (50nm) was deposited on the Ag surface via sputtering. The deposited thin films were finally backed with 54 μ m Pb based paint by means of a mechanical process with a hand coater. The reflectors showed no sign of degradation after one week exposure to air prior to paint backing. The reflectors so fabricated were characterized for compositional, structural, morphological and optical properties using scanning electron microscopy (SEM), energy dispersive (X-ray) spectroscopy (EDS) and optical spectroscopy. The observed reflectance from the spectroscopy analysis showed high reflectance of 98 – 99% at wavelength band of 400 nm – 700 nm which is ideal for concentrated solar (thermal) power (CSP) applications.

Keywords Physical vapour deposition, Concentrated solar thermal power, Thin film and nanoscale coating

1. Introduction

Reflectors are one of the most important components of a concentrated solar (thermal) power (CSP) technology. The manufacturing of this CSP component is currently a great challenge facing the technology because developing a CSP reflector with high reflectivity and uniform coatings remains an upheaval task in the industry.

Achieving an ideal CSP reflector will help to ensure that CSP as a source of power becomes sustainable; this is because with such reflectors, the current high cost of electricity from CSP will be drastically reduced. This is so because such reflectors can withstand the adverse environmental conditions and, at the same time, achieve high reflectance of about 100% (Bhattacharya *et al.*, 2012; Hatwaambo *et al.*, 2009).

CSP is one of the emerging solar energy technologies. Its applications range from electricity generation, solar cooking, industrial heating, solar drying, solar ponds, solar chimney, solar air-conditioning and solar chemical synthesis (Fernández-García *et al.*, 2010; Thirugnanasambandam *et al.*, 2010; Barlev *et al.*, 2011, Ahmad *et al.*, 2014 and Nwosu,

2015). This technology today is one of the mainstay of electrical power generation in Spain, USA and India (Mills, 2004; Pavlović *et al.*, 2012; Baharoon *et al.*, 2015 and Papaelias *et al.*, 2016). Having observed the great potentials of this technology in the nearest future and its hope to curb the world energy crisis especially in Africa and parts of Asia, some countries of the world, including Nigeria, are now working towards domesticating this free source of energy.

With CSP, it is envisaged that the world energy crisis will soon be over; with the adverse effects of climate change and global warming curbed since no CO₂ emission is traceable to this technology (Pavlović *et al.*, 2012) as CSP is known to be one of the most environment friendly sources of energy.

Usually, good reflectors are expected to produce very high reflectance with low absorptance at a very low cost. The most common CSP reflectors obtainable today are silver and aluminium based. Silver based reflectors possess some characteristics that make them special. These include high optical reflectance of 97% and above (compared with aluminium which has reflectance of 91 - 92%) within the wavelength band of 300 < λ > 700 nm (Hass and Waylonis, 1961; Ehrenreich *et al.*, 1963); very good specularly such as durability and ability to resist distortion from forces compared to other glass mirror reflectors; and tolerance to impurities and mirror compositional variations (Czanderna and Masterson, 1985). Silver based reflectors are usually concealed with layers of Cu and paint deposits to prevent

* Corresponding author:

michaelonuu@yahoo.com (Michael U. Onuu)

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them from degradation (IEA, 2010; Ummadisingu and Soni, 2011).

Various techniques have been adopted in the past for the production of CSP reflectors. They include: electroless deposition method (EDM), chemical vapour deposition method (CVD) and physical vapour deposition method (PVD) (Babolan, 2005; Salas *et al.*, 2012; Sutter *et al.*, 2013). Some of these methods pose certain coating challenges like poor uniformity, poor bonding and specimen contaminations (Nahrstedt *et al.*, 1996), with the exception of PVD which has been observed to perform optimally especially in solar reflectors coating (Kennedy and Price, 2005; Atkinson *et al.*, 2015; Nwosu, 2015).

In this work, asilver thin film reflector backed with Cu and Pb paint was fabricated. This novel silver reflector has shown optimal performance because of the nanoscale coatings employed and recommended for CSP reflectors manufacturing.

2. Experimental Details

2.1. Glass Substrate Preparation

Prior to coating, the 1 mm glass slide substrates used in the investigation were properly cleaned to ensure the removal of dirt, grease, silica gel hydroxyl layer, finger prints and other contaminants from the glass surface. This is necessary in order to prevent poor bonding/adhesion of the coating.

Ultrasonic cleaning device (**Figure 1**) with frequency as high as 18 kHz was used for the cleaning. First, the glass substrates were inserted into a glass rack after which they were immersed into reagents in a beaker (**Figure 2**).



Figure 1. Precision ultrasonic cleaning device

The glass substrates were initially immersed in a washing-up liquid (made up of 1 ml of solvent + 399 ml of tap water) for 5 minutes in a sonic bath, after which they were rinsed in tap water. The substrates were later immersed in de-ionised water (400 ml) for 5 minutes in sonic followed by 10 minutes ultrasonic bath in 400 ml each of acetone, general purpose Isopropanol (IPA) and pure IPA, respectively. Thereafter, the glass substrates were annealed

in air at 100°C; this was to ensure that the substrates were free from moisture prior to coating.

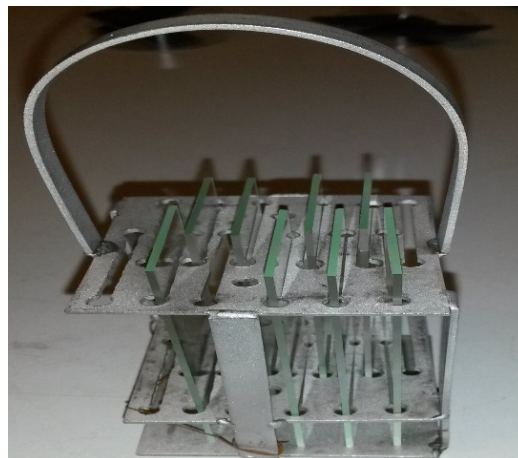


Figure 2. Microscopic glass rack

The uncleaned glass substrate contains a lot of debris compared to the cleaned glass substrate as shown in **Figure 3**, and **Figure 4**, respectively. Thus, the surface smoothness and cleanliness of the glass substrate determines. To a large extent, the nature of the coating to be deposited. **Figure 5** is a flow chart that illustrates the glass substrates cleaning process.

2.2. Silver Thin Film Deposition

Thermal evaporation (a PVD technique) was employed in the deposition of Ag thin film. Silver metal utilised in this study is the 0.25 mm Ag wires (AGE406) of 99.99% purity from Agar Scientific, United Kingdom (UK). Prior to coating, the Ag wire was first weighed for each run with Sartorius electronic weighing balance. This process was applied to each experimental trial in order to determine the actual weight for the desired thickness to be deposited.

The Ag metal coatings were deposited at a current of 0.2 A with the evaporating boat with melting temperature range of 1400°C – 1800°C. These temperatures are high enough to melt the Ag lumps as the melting temperature of Ag is known to be 192°C (Silver, 2015). Four different samples (X1 X4) were prepared (**Table 1**) with the appropriate calibrated thickness of 100 nm Ag deposited (**Figure 6 and Figure 7**). The weight of the Ag was determined using Sartorius electronic balance prior to deposition, after which the thickness of the film was analysed with Dektak surface profiler.

Sequel to the actual Ag coating as presented in Table 2, trial/calibration coatings were first carried out. From these trials coatings, it was deduced that as the weight of the Ag metal increases, the thickness of the Ag coating also increases (shown in S1.....S4); this is shown in **Table 2**.

From **Table 2**, it is shown that for thermal evaporation, growth rate (Gr) is dependent on the weight of material to be deposited (Wm).



Figure 3. 120μm SEM micrograph of uncleaned glass substrate @120 magnification (scale bar: 250μm)

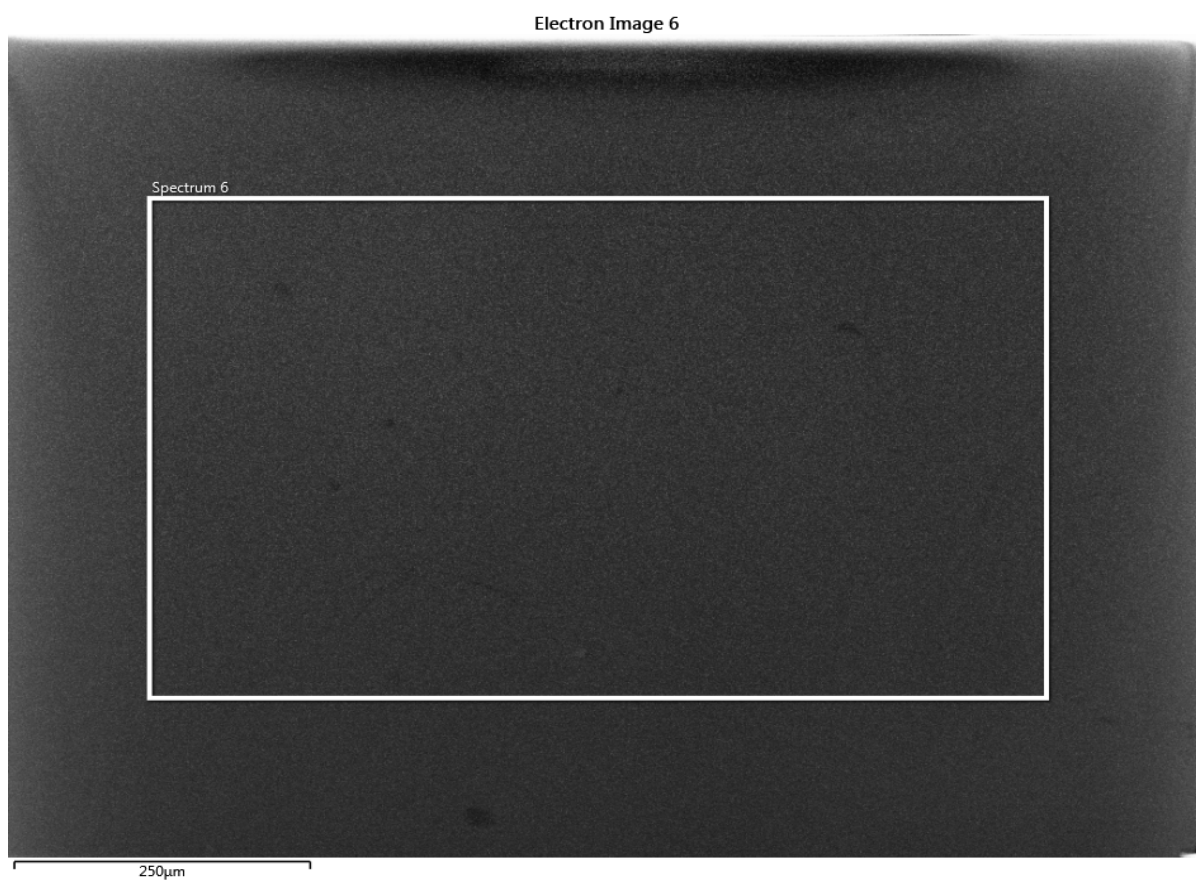


Figure 4. 120μm SEM micrograph of cleaned glass substrate @120 magnification (scale bar: 250μm)

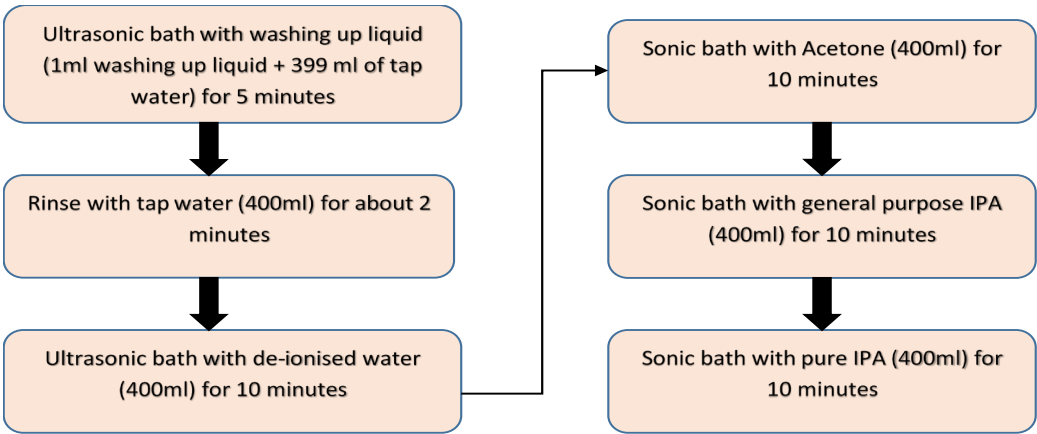


Figure 5. Process flow of the glass cleaning

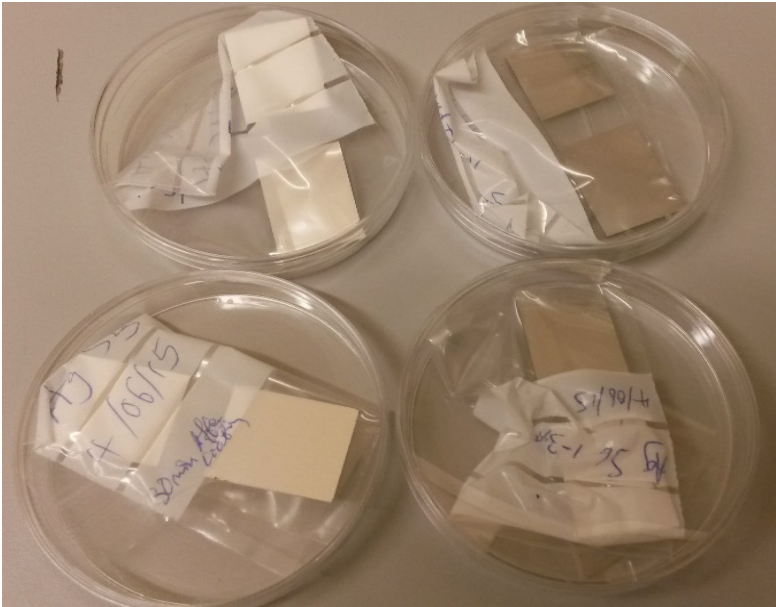


Figure 6. Silver coating at 100 nm film thickness

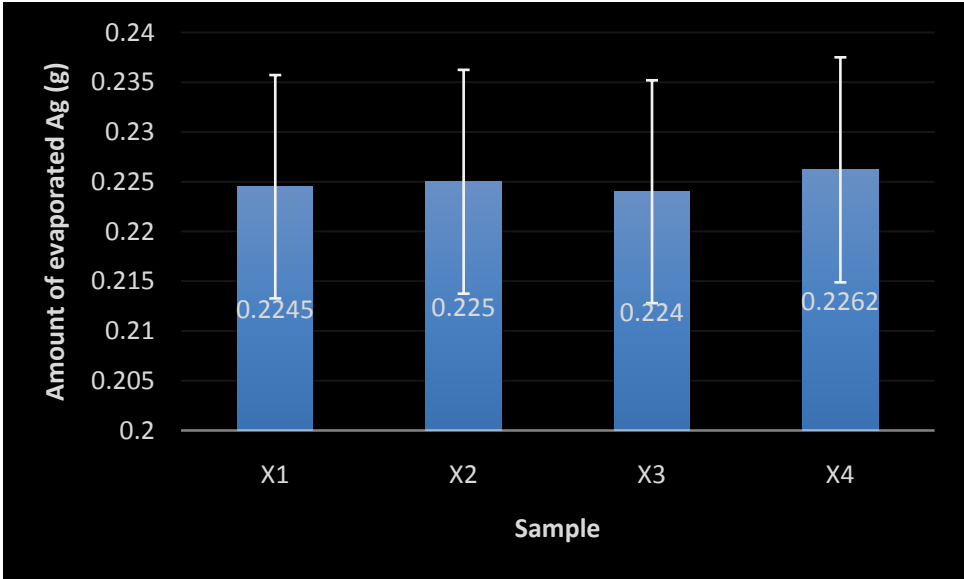


Figure 7. Mean deviation/Error bar plot of evaporated Ag

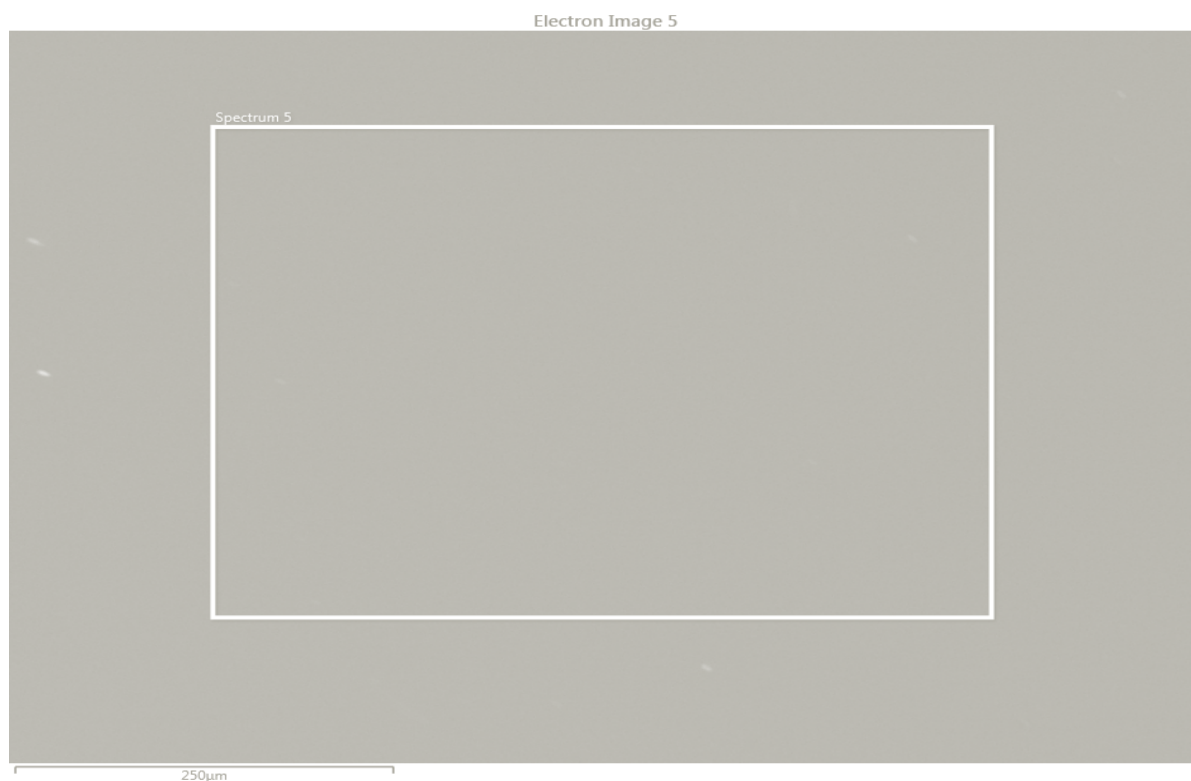


Figure 8. SEM Micrograph of Ag surface analysed same day after coating 250µm @ 150 magnification (scale bar: 250µm)



Figure 9. SEM Micrograph of Ag surface analysed 1 day after coating 250µm @ 150 magnification (scale bar: 250µm)

From **Figure 8** and **Figure 9** it is clearly seen that the Ag surface did not tarnish even after one day exposure without any protective overcoat. This entails that PVD technique employed for the Ag deposition is quite novel.

2.3. Copper Thin Film Deposition

Sputtering was adopted to deposit Cu thin film onto the Ag coated surface using 99.99% pure copper target (AG 8077) purchased from Agar Scientific, UK. The first set of Cu deposition was carried out in order to determine the growth rate; this run lasted for 45 minutes resulting to thickness

yield of 1700 nm (measured with Dektak Profilometer). This 1700 nm-Cu film suffered severe delamination (**Figure 10**). This might be due to stress build-up, and hence it is not advisable to deposit very thick films unto glass reflectors, as this will encourage poor adhesion and bonding of the Cu film with the substrate.



Figure 10. Copper coating delamination at 1700 nm film thickness

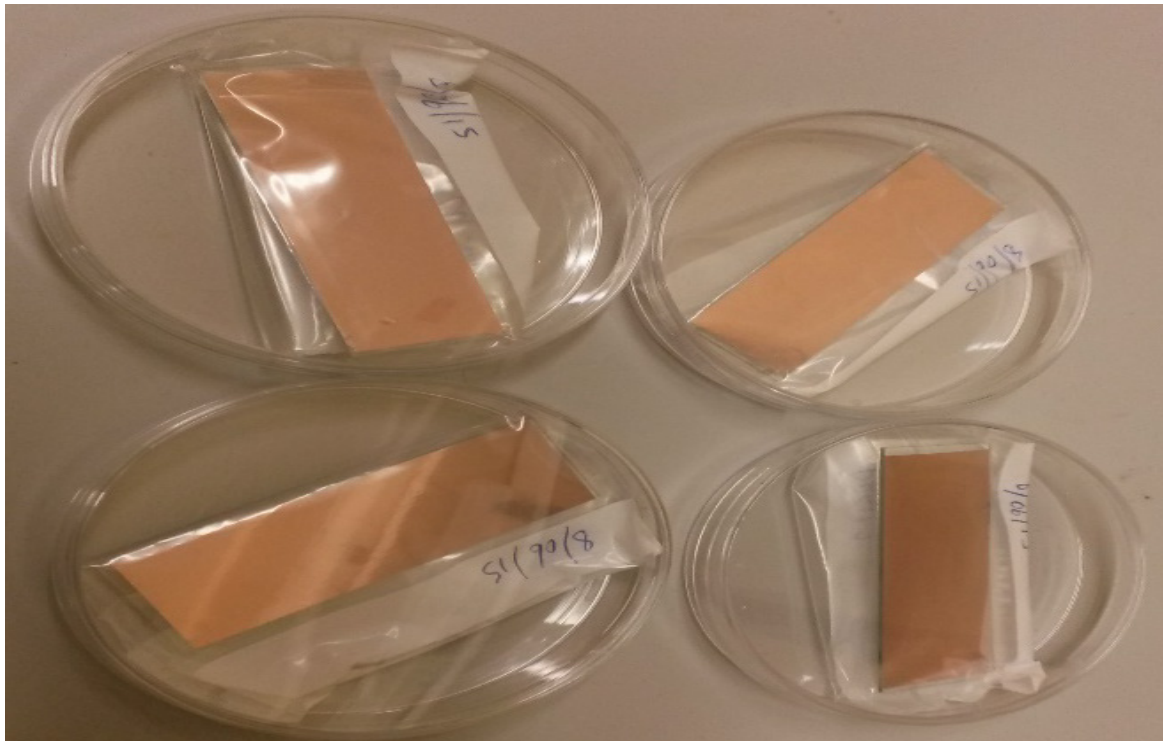


Figure 11. Copper coating at 50 nm film thickness without any delamination

Table 1. Silver deposition thickness obtained for different sample runs

Runs	Sample	Ag (g)	I (A)	Thickness (nm)
1	X1	0.2245	0.2	100
2	X2	0.2250	0.2	100
3	X3	0.2240	0.2	100
4	X4	0.2262	0.2	100

Table 2. Silver deposition trial coatings

Trial Runs	Sample	Ag (g)	I (A)	Thickness (nm)
1	S1	0.0598	0.2	77.0
2	S2	0.1100	0.2	88.0
3	S3	0.2198	0.2	100.0

Following the growth rate computation, it was found that 80 seconds is required to deposit 50 nm film, which is the range of Cu thickness required for the solar mirror reflector that will be free from delamination as shown in **Figure 11**.

Both the thermal evaporation of Ag and sputtering of Cu were carried out using Leybold (L560) PVD coating machine.

2.4. Paint Deposition

In order to protect the developed mirror (reflectors) coatings, Pb based paint was employed to back the coated Cu layer. The paint deposition was carried out in a fume hood using a hand roller of 24μm pitch. Paint thickness of 54μm was deposited as measured with Dektak® Profilometer. The percentage of Pb in the paint was confirmed to be 7.5% using EDS elemental mapping (**Figure 12**). The choice of Pb paint as the reflector backing material was due to the perceived ability of Pb to withstand corrosion.

3. Results and Discussions

3.1. Compositional, Structural and Morphological Properties

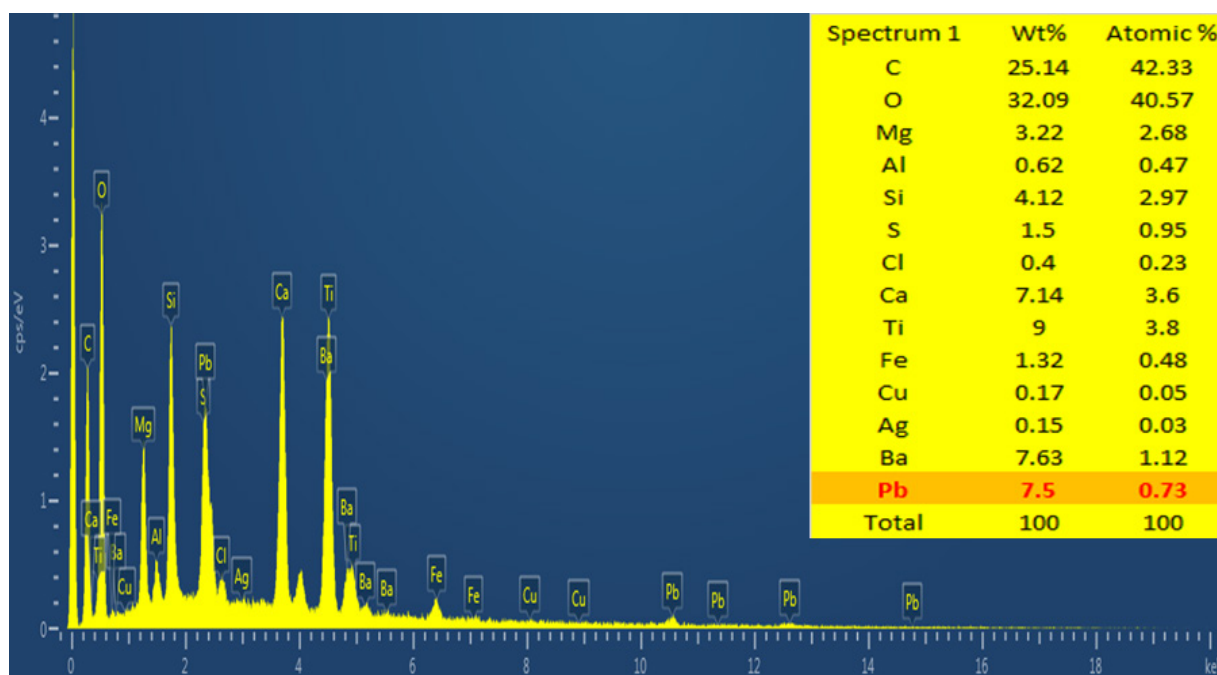
The elemental mapping of the chemical constituents of the coated reflector samples was carried out using EDS. The physics of electron emission described by Max Planck is the basis for the EDS spectral composition analysis (Almanza *et al.*, 1992; Feng *et al.*, 2003; Wasa *et al.*, 2004; Kennedy and Price, 2005 and Dobrzański *et al.*, 2007).

Since each chemical element has its characteristic emission line spectrum, the line spectra is determined by the energy levels present. **Figure 12** also shows the EDS micrograph of the coating with the presence of Ag, Cu and about 7.5% of Pb recorded; the other elements present were due to the glass substrate (as shown by high % of Si) and the paint composition.

Figure 13 shows the structural micrographs of the coated reflectors obtained using high resolution SEM capable of producing 1 nm image magnification. The carbon present must be due to the graphite tape used on the sample prior to loading to ensure that it gets charged for the SEM/EDS analysis. With SEM many samples can be focused at the same time due to its large depth of field, H, usually represented as given in equation 1:

$$H = \frac{\theta \cdot wd}{A \cdot M} \quad (1)$$

where: θ = minimum distance the eye can focus on photograph (m); Wd = distance between the lens and specimen (m); M = selected magnification; A = selected aperture (f/D).

**Figure 12.** EDS elemental mapping showing 7.5% of Pb in the paint composition

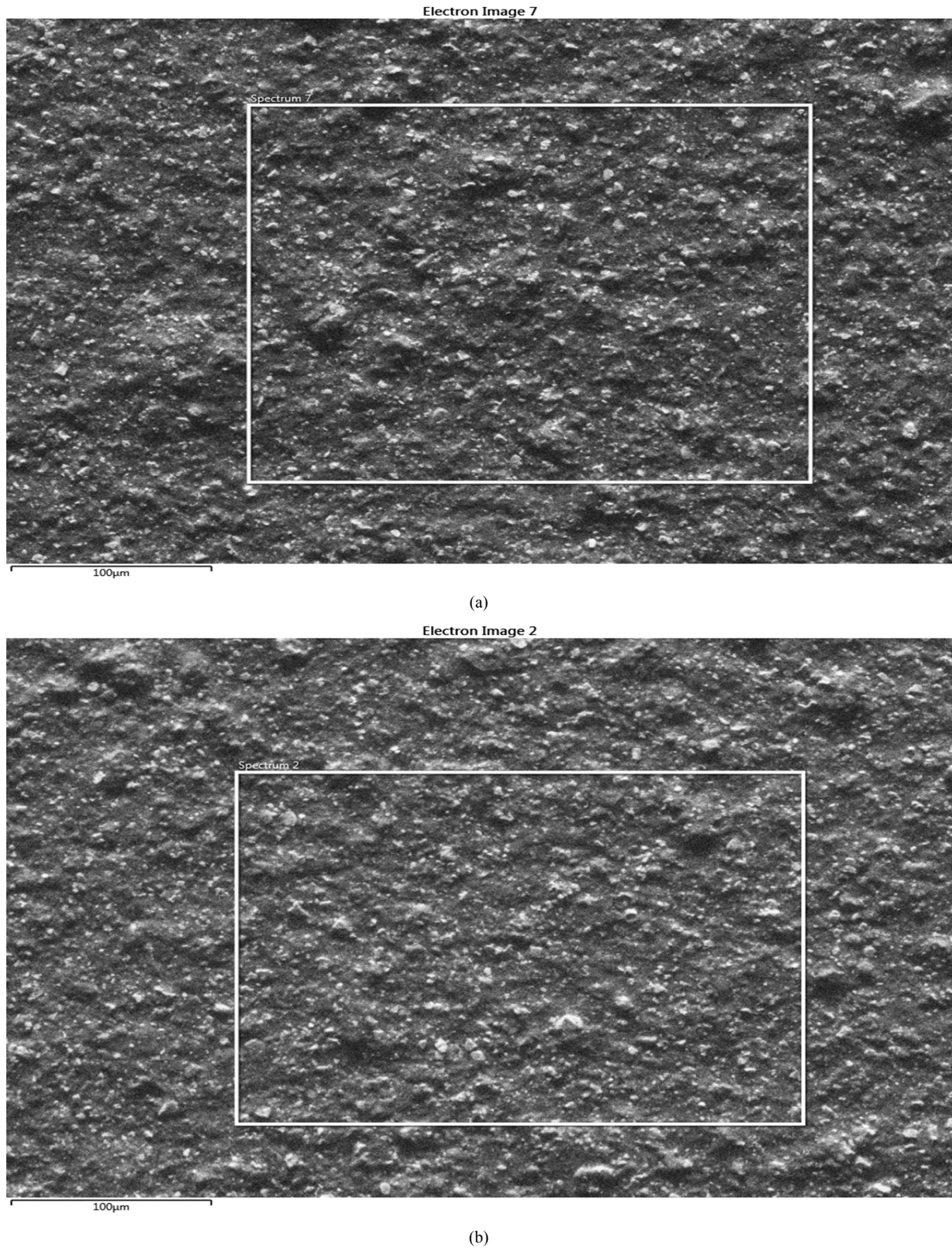


Figure 13. SEM micrograph of the coated reflector samples (a) and (b) at 250 magnification (scale bar: 100µm)

The SEM micrographs obtained (**Figure 13**) showed a well-defined smooth surface topography, boundaries and uniform grains, indicating structural homogeneity. This however confirms the statement by some authors that PVD coating produces a very good coating on glass (Babolan,

2005; Salas *et al.*, 2012). The SEM employed for this analysis is Philips XL-30 ESEM which has high-brightness field emission gun (FEG) that operates from 200V to 30kV, hence capacity to image any sample except very large samples and volatile liquids and gases. This machine is also

capable of detecting EDS of samples; hence in this work it was employed for both the SEM micrograph imaging and x-ray diffraction (XRD) analysis.

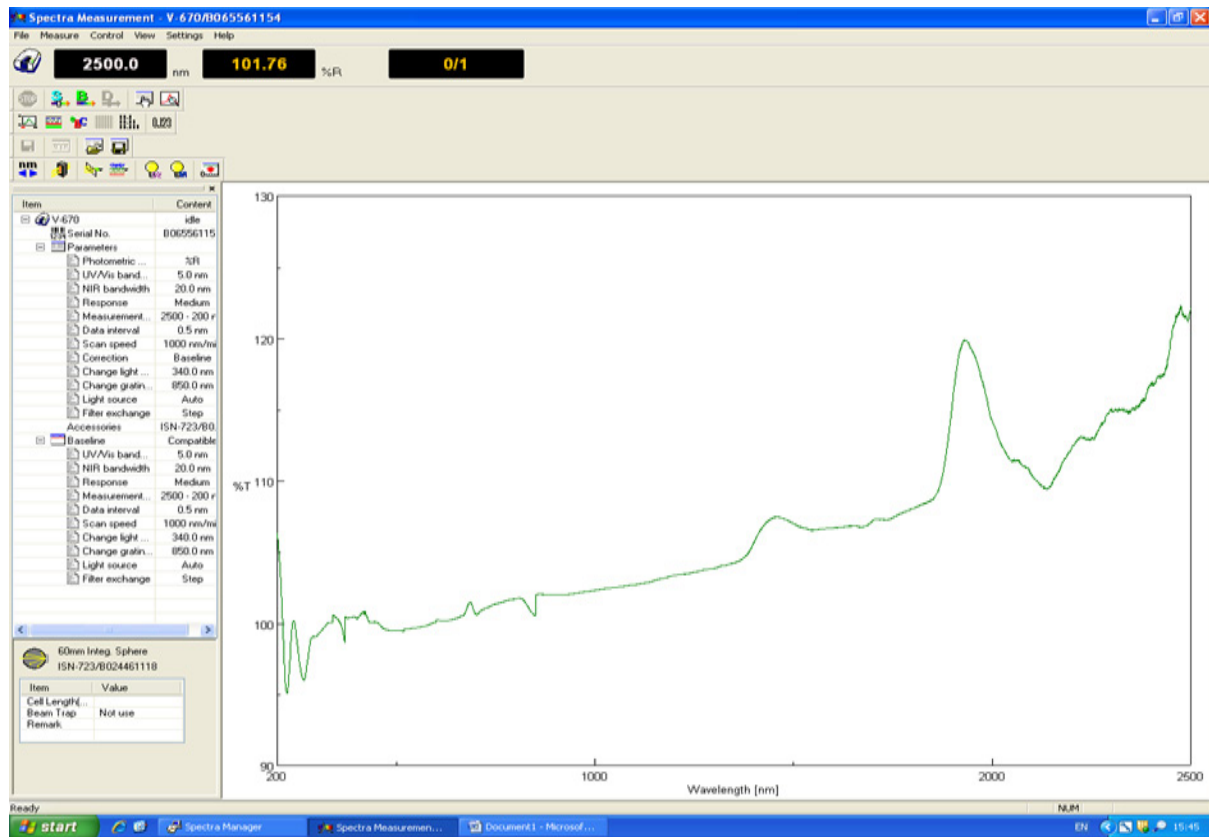


Figure 14. Reflectance baseline measurement with spectral on white plate

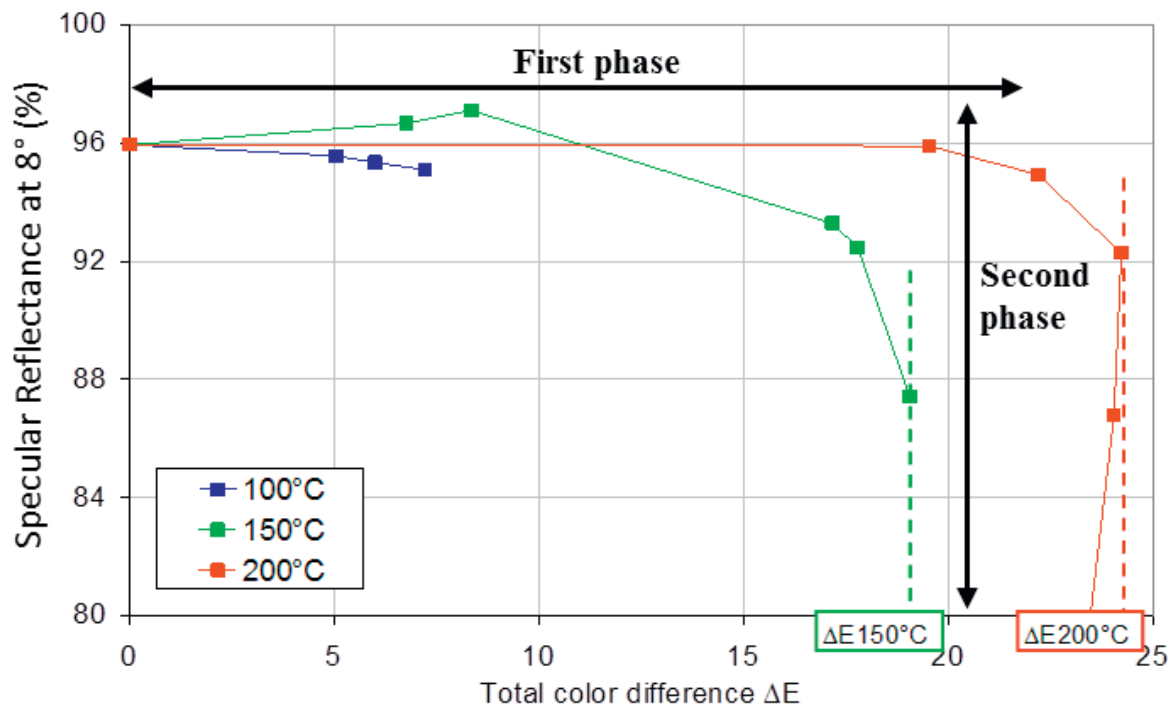


Figure 15. Reflectance of a silver coated reflector as a function of colour change, ΔE (Raccurt et al., 2014)

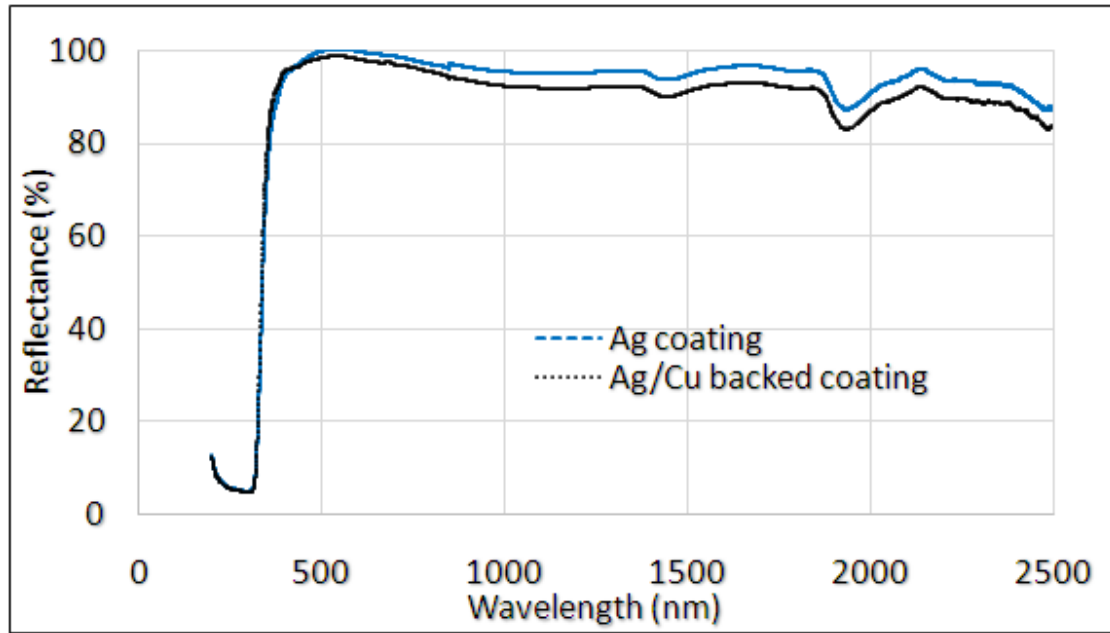


Figure 16. Ag coating and Ag/Cu backed coating reflectance

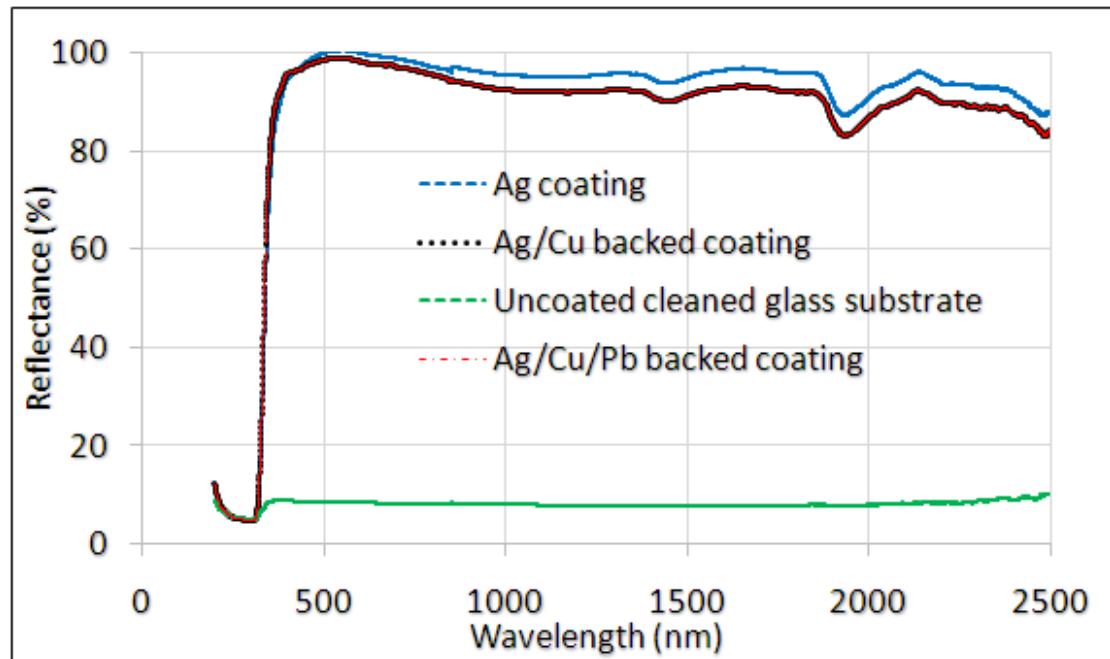


Figure 17. Ag/Cu/Pb backed developed reflectance

3.2. Optical Properties

The optical characteristics of the developed solar reflector were analysed using V670 (UV/VIS/NIR) Jasco spectrophotometer. The principal property investigated is the reflectance (reflective performance) of the reflector. The optical measurement covered wavelength spectra of 200 nm – 2500 nm (i.e the ultraviolet, visible and near infrared band spectra). A 60 mm integrating sphere holder was used for measuring the reflectance. The actual reflective ability of the mirrors were recorded after taking the baseline measurement (*Figure 14*) by positioning a standard spectralon white plate

into the light propagating part of the sphere.

Subjecting the reflector samples to heating at various temperature can lead to colour change as well as loss in reflectance (*Figure 15*). According to Raccurt *et al.* (2014), this colour change can occur in two degradation phases; for the first phase, reflectance is stable as the colour changes. The change in colour is probably because of the paints degradation, as the paint gradually turns powdery and porous which creates micro holes leading to the diffusion of oxygen to the silver layer. Under the influence of oxygen, the second phase of degradation is established. In this second phase, the silver layer starts to corrode which then leads to the sharp

decrease in reflectance, hence can drastically reduce the mirrors lifespan.

The overall reflectance obtained from the reflectors was quite encouraging as about 98 – 99% was achieved in this work (**Figures 16** and **17**). This shows an improvement on already commercially available CSP reflectors as illustrated by Alcañiz *et al.* (2015) and implies that PVD technique, especially the novel combination of thermal evaporation of Ag and sputter deposition of Cu employed in this work, is a promising combination required to achieve very strong bonding with high reflectance needed for the advanced CSP reflectors, which is in agreement with the findings of Atkinson *et al.* (2015).

Also the smoothness of the reflectance curves conforms to the smooth structural micrographs obtained with the SEM; notwithstanding, the deposition of Pb paints using the threaded hand rollers exposed some parts of the Ag layers micro voids. This might encourage corrosion of the reflectors in the future which might lead to a drop in reflectance as highlighted by (Brogren *et al.*, 2004). Hence new techniques need to be adopted in future for the reflector paint backing.

Figures 16 and **17** show continuous drop in the reflectivity of the Ag coating on backing with Cu and also backing with Pb paint within the wavelength range of 470nm – 2500nm. This drop might be attributed to inter-layer diffusion of Cu atoms into Ag layer. Also as observed in **Figure 17**, the maximum reflectances produced by the uncoated cleaned glass substrate were 8.80% (400 nm) and 8.20% (700 nm), compared to the Ag coating, Ag/Cu and Ag/Cu/Pb backed coating which produced high reflectances of 96% (400 nm) and 99% (700 nm) of the solar band spectrum.

4. Conclusions

In conclusion, a quite novel Cu and Pb paint protected Ag thin film reflector was successfully fabricated. The Ag thin films were deposited on the cleaned glass substrate using thermal evaporation while the Cu thin films (protective-backing) were deposited on the Ag layer via sputtering; and the Cu layer finally sealed with Pb-based paint as an anti-corrosive layer. Spectral analysis of the developed reflectors' optimised structure of glass/Ag (50 nm)/Cu (100 nm)/Pb-paint (54µm) showed high reflectance of 96 – 99% within the electromagnetic band spectrum of 400 – 700 nm. This nanoscale coatings have demonstrated the potential application of the reflector in concentrated solar thermal power manufacturing.

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