# *Appendix A*
# Silver thin film coating on reflector surface of radiation Calorimeter (RADCAL)

## A.1 introduction

In the radiation calorimeter, the reflector surface arrangement is made to reflect the incoming radiation to the absorbing surfaces. The reflector surface should be as nearly ideal and thus, a stable reflector coating should be optimized for the entire solar spectral region i.e., 0.3 µm to 2.5 µm wavelength range. It can be achieved by the selected metallic surfaces such as aluminum, silver, and gold. However, aluminum reflecting surfaces may not withstand the environmental conditions such as reaction with ambient oxygen and moisture, which usually led to the degradation of reflecting surfaces. In contrast, gold is very stable under open environmental conditions, but relatively very expensive and that's why not considered as a common reflecting surface. Silver has been a common choice for reflecting surfaces not only because of its environmental inertness but also the relatively better-reflecting properties ~95 – 99% [Moreno et al., 2005, Lide, 2004, Rancourt, 1996] for the solar spectral region, comparable to that of gold reflecting surfaces 98 – 99% but at a higher wavelength (≥ 0.5µm) and better than aluminum reflecting surfaces 87 – 93%. Considering the pros and cons of reflecting metals, silver thin film is optimized as the reflecting surface for the reflector region of radiation calorimeter.

## A.2 Experimental detail

The thin film of silver (Ag) is deposited on a cleaned Cu flat substrate using thermal evaporation technique. The deposition conditions were optimized to get the film with optimum optical reflectance. The deposition detail is given in section 3.2.1.1. **Figure A.1** shows the reflector surface after silver (Ag) deposition.

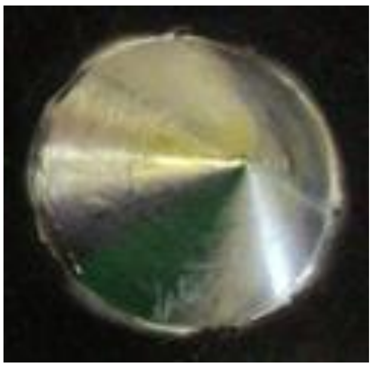

**Figure A.1** Optical image of silver deposited conical reflector surface

## A.3 Result and discussion

The recorded X-ray diffraction results are shown in **Figure A.2** for the thin silver film optimized on a copper substrate. The observed diffraction peaks at 2θ = 37.7˚, 43.8˚, 63.7˚ and 76.4˚ can be indexed with the reference ICDD PDF No. 03-065-8428, corresponding to (111), (200), (220) and (311). Cubic crystallographic planes of the face-centered, respectively, as shown in **Figure A.2**. The XRD measurements suggest the presence of a thin film of metallic silver on copper substrates.

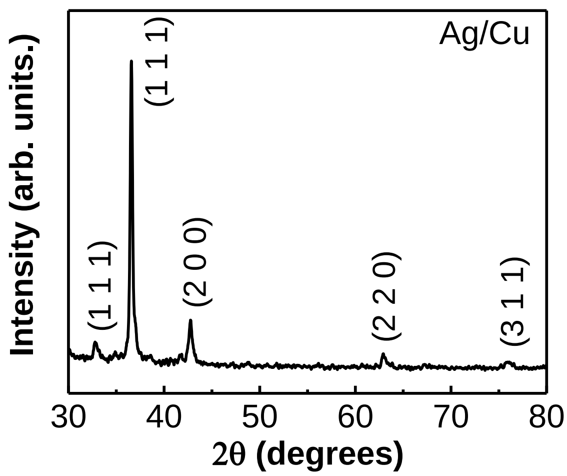


**Figure A.2** The XRD spectrum of Ag thin film coated on the copper substrate (Ag/Cu)

Scanning electron micrographs (SEM) for Cu substrate and Ag / Cu were recorded. They are illustrated in **Figure A.3** with optical images. Optical images do not show surface roughness or treatment footprint, as shown in **Figure A.3(a & b)**. However, the micrographs corresponding to the SEM clearly show the traces of the cleaning process on the copper substrates **(Figure A.3(c & d))** that are also present in the support on thin layers of silver deposited shown in the right panel of **Figure A.2**. Inset of **Figure A.3(d)** shows the EDX measurement of Ag / Cu structure, indicating the presence of only a fraction of silver and copper from the substrate. No oxygen measurement was found in the EDX measurement, which suggests the deposited silver thin film is metallic. Also, scanning probe measurements using AFM were performed to study the surface micrograph of copper and silver-coated copper substrate. **Figure A.3(e& f)** shows the captured topographic image of copper and silver-coated copper substrate, respectively. The surface roughness (Rq) (RMS) for the scanned area is estimated using equation (4.1)

$$Rq = \frac{1}{L}\int_0^L \left|Z^2(x)\right| dx \qquad \text{A.1}$$

Where Z (x) is describing the profile of the surface of the sample along the length studied L [Oliveira et al., 2012]. The observed surface roughness for the silver deposited sample was approximately 16.74 nm, which is about half compared to pristine copper substrate surface roughness of approximately 32 nm. This reduction in roughness after the deposition of a thin film of silver is attributed to the smoothing of the ditches of the substrate after the deposition of a thin film of silver. This roughness of the silver surface is much smaller compared to the wavelength of the incoming solar spectrum. Therefore, the reflective properties of the Ag / Cu surface are preserved.

The absorptance of fabricated Ag / Cu thin film was estimated by recording the reflectance in the UV-Vis range (0.2 to 0.9 µm). **Figure A.4** represents the measured reflectance for fabricated silver thin films on the copper substrate. The reflectance of the film thickness of

100 nm is equivalent to approximately 60% in the measured range, shown in **Figure A.4**, called a pre-optimized sample. This low reflectance is due to the surface irregularities present on the deposited Ag/Cu thin film. Given the low reflectance, the thickness of the thin silver film increases to 500 ± 15 nm as the deposition time increases to 30 minutes for identical conditions. The number of samples is prepared, and the reflection factor recorded is shown in **Figure A.4** for samples of a greater silver thickness (500 ± 15 nm). These samples have a higher reflectivity of ~ 87.29% ± 4% in wavelength range > 0.3 μm. The increase in the reflectance for 500 nm thick silver deposited sample compared to 100 nm thick silver deposited sample is due the low surface roughness ~ 16.74 ± 1.00 nm of thicker sample (500 nm) as compared to the higher surface roughness ~ 28.39 ± 1.83 nm of thin (100nm) silver film. It indicates that the improvement in reflectance after increasing the thickness of the film is justified **(Figure A.3 (e & f)).** Also, there is a significant drop in reflectance ~ 0.3 microns was observed, and this is attributed to the silver plasmon resonance absorption due to the large free electrons (~ 1022 cm$^{-3}$) in silver [Oliver, 2013]. The overall reflectance of the deposited film would not be affected due to plasmonic absorption as the solar spectrum mainly lies above 0.3 μm. The inset plot of **Figure A.4 (a)** shows the measured reflectance with thickness. The reflectance of the deposited silver film is matching with reported literature [Fekkai et al., 2014, http://www.filmetrics.com/reflectance]. The small difference observed in reflectance values can be attributed to slight differences in surface properties, such as roughness, which depend on the surface quality of the substrate and the process adopted to deposit the silver layer on the substrate. These 500 nm thick silver film deposits are made on a flat copper substrate. The inclined copper substrate is also utilized for deposition of silver reflecting surface under identical conditions for the conical reflector of RADCAL, and around 500 nm thick silver reflecting layers are deposited on different samples. The recorded reflectance is shown in **Figure A.4(b),** and results show similar spectral reflectivity observed with deposition on flat copper substrates see **Figure A.4(a)**. These observations show that there is no significant change in the spectral reflectivity of the silver layers and that the spectral reflectivity is relatively insensitive to substrate geometry in the area of vapour coverage. Finally, the silver reflective layer is deposited in RADCAL for identical deposit conditions. Inset image of **Figure A.4(b)** shows silver deposited conical reflective surface.

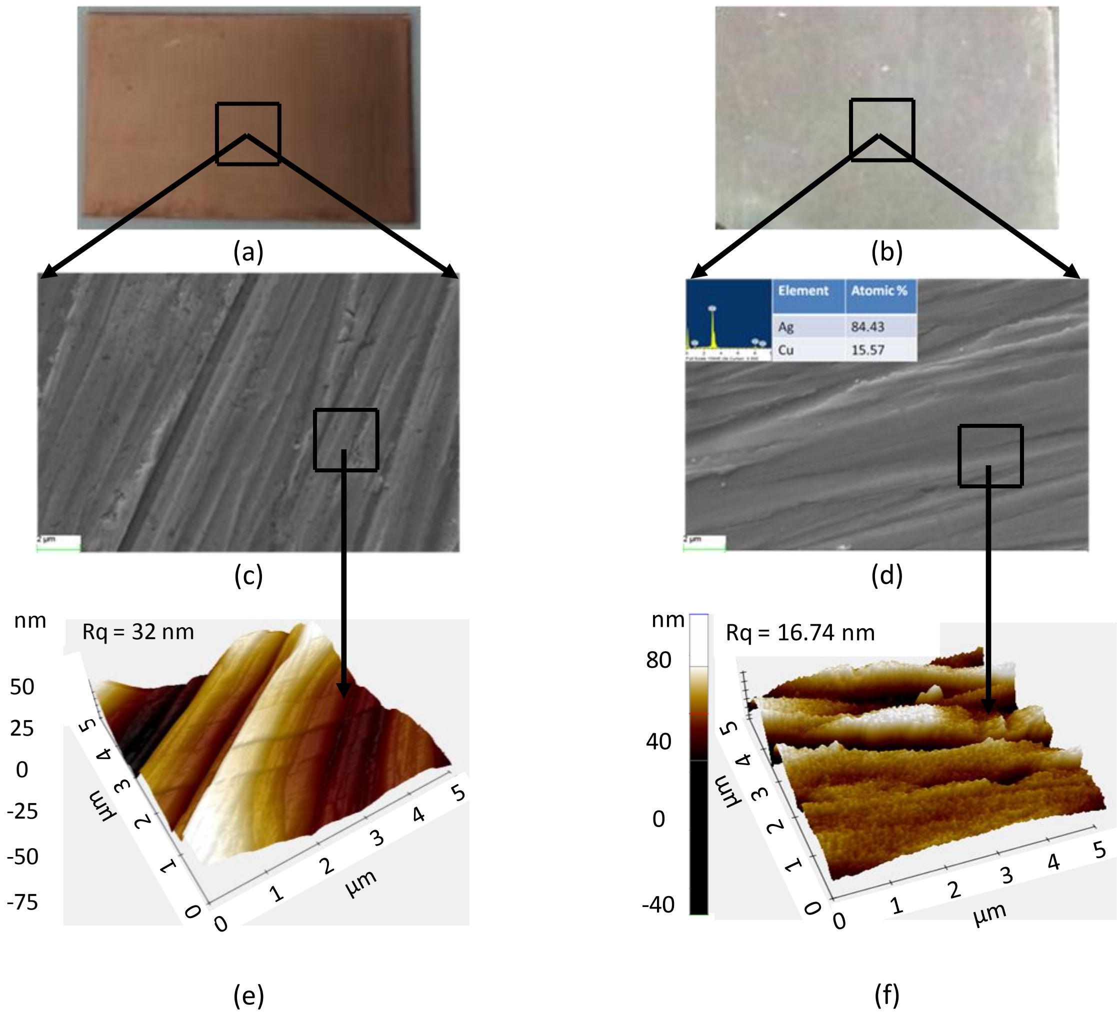


**Figure A.3** (a, b) Camera image (c, d) SEM image (e, f) 3-D AFM image of pristine copper and silver deposited copper

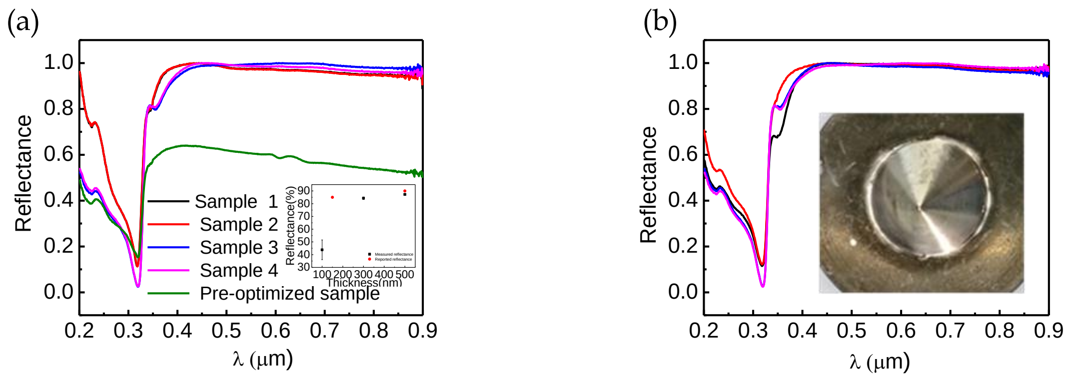


**Figure A.4** Reflectance versus wavelength plot of (a) Ag/Cu (flat surface) (b) Ag/Cu (inclined surface) [inset: camera image of conical reflecting surface.]

## A.4 Conclusion

The deposition conditions are optimized for the maximum reflectance and used to deposit silver thin films on reflector surface of the radiation calorimeter (RADCAL). The reflecting surface coated with 500nm thick silver metallic film showed the optimum reflectance ~87% in UV-Vis range.