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Investigation of the Statistical surface morphology and optical properties of the Ag/Al and Ag/Cu thin double-layers

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Abstract: In this work, thin films were deposited on the amorphous glass substrates by magnetron sputtering method. Surface morphology of double-layers of Ag/Al and Ag/Cu were investigated. For surface morphology studies atomic force microscope (AFM) and scanning electron microscopy (SEM) were used, variations of the grain and partical size as well as surface roughness, roughness exponents and correlation length were studied for double layers. Coating Cu and Al on silver thin films reduces the surface roughness and correlation length but when Ag is deposited on Al and Cu correlation length increases. The reflectance is measured in wavelength range of 200-1100 nm, and deposition of Cu and Al thin films on Ag film causes variation on the amount of the reflectance drastically.

Keywords: Ag/Al double-layers, Ag/Cu, Reflectance, correlation length, surface roughness.

1. Introduction

In recent years, interest in nanostructured metal thin film has increased due to their remarkable optical properties and tremendous increase in potential applications, which include ultrafast optical switches, optical tweezers, labels for biomolecules, optical filters, biosensors, surface enhanced spectroscopies [1], plasmonics [2] and chemical sensors [3-5]. Among all the metals, Ag and Au have attracted much interest due to their unique optical properties [2-4,6-8]. Silver nano layers have the highest reflectance and the lowest polarization for the full IR region and down to a wavelength of 400 nm, a very low absorption in the visible wavelength region. Normally a thin Ag film is used in the transparent heat mirrors to ensure the high reflection in the infra red spectral range [9,10]. The disadvantage of silver is, it does not have a high reflectance at wavelengths below 400 nm, there is a minimum reflectance at 320 nm due to a surface plasmon resonance [11]. The Ag metal nanoparticles exhibit local surface plasmon resonance (SPR) due to the interaction of incident electromagnetic radiation with surface electrons. The most important aspect is the ability to tune the SPR wavelength for various applications of metallic nanoparticles [7,9,10]. Another problem is silver thin films is agglomeration of Ag films, and It is essential to suppress agglomeration of Ag films which is caused by thermal treatment for their successful application as new metallization materials. One of the solutions is considered to be alloying silver with other metals. An improvement in the use of Ag (Al) films has recently been reported [12]. Previously, reported the usefulness of a Ag–Ni film, also Al and Au were selected as a new alloying element for agglomeration suppression [13]. The Ag thin film tarnishes under ordinary atmospheric conditions and the weak adhesion of Ag thin film on to the dielectric and glass substrates also is a major problem. In some reaserchs, sandwiching the Ag layer between two thin films of different metals for example Ni, Al, Ti, …showed reduction of tarnishing and improved adhesion of Ag. The surface, which is the first interface of the material, has an important role in the interaction between the material and the environment and with other materials and radiation. Surface roughness has an enormous influence on many important physical phenomenas such as mechanical contact, sealing, adhesion, wave scattering and friction. The most of the surfaces in nature are rough in some degree, and this fact is a motivation that can be studied as a random process. In fact, a surface for a special application requires specified statistical properties. Correlation between the optical properties and surface morphology can be determined from measured optical and statistical parameters (roughness and correlation length). In most of the previous works the synthesis of Au–Ag, Ni – Ag, Cu-Ag, Al- Ag alloy bimetallic have been reported [5,8,13-16], but in this work investigation of the effect of the Ag/Al and Ag/Cu thin double-layers on the optical and morphological properties of these nano layers were carried out. Thin films were deposited by DC magnetron sputtering on glass substrate. This deposition technique presents interesting advantages such as high deposition rates, low substrate temperature, good adhesion of thin film to glass substrate, and finally, films with good packing density. To investigate the surface morphology of these thin films, atomic force microscopy (AFM) and scanning electron microscopy (SEM) were employed. Surface roughness, roughness exponents, correlation length were studied, and the variation of the reflectance in these double layers in wavelength of 200-1100 nm were investigated.

2. Experimental Work

Thin films of Ag, Al, Cu were prepared by DC magnetron sputtering (Hind High Vacuum, H.H.V, 12"MSPT) on glass substrate. The vacuum system could provide base pressure of 10-6 -10-7m.bar thus background pressure prior to thin film deposition was around this value (10-6 mbar). A circular flat disc of Ag, Cu, Al (99.9% purity) with 3 mm in thickness and 125 mm diameter were used as target (cathode). Ag, Al, Cu thin films were produced in research grade Ar (99.99% purity) atmosphere which was used for plasma formation .In this work Ar pressure was 0.02 m.bar. Circular glass substrate with 25 mm diameter and 1 mm thickness was used. Just before using these glasses they were cleaned in heated acetone and then by isopropyl in ultrasonic bath for 2 minutes. Substrate temperature was monitored during deposition by a digital thermocouple which was placed on substrate holder, since period of coating for each sample was relatively short, so substrate temperature did not changed during deposition (namely 300 K). For measuring deposition rate and thickness of Ag, Al, Cu thin films a vibrating quartz crystal thickness monitor was employed. The distance between target and substrate was maintained at 12 cm for all the depositions. Surface morphology of these thin films on a small scale (< 5 μm) was imaged using atomic force microscopy (Park scientific AFM Auto Probe model CP) and AFM images were employed using force constant mode and digitized into 256×256 pixels. All AFM images were acquired in ambient air. For a better comparison of the effects of different interfaces, we kept all other experimental parameters unchanged. To analysis the AFM images, the topographic image data were converted into ASCII data. Scanning electron microscopy (SEM) of the produced samples also was carried out (Hitachi SEM model S-4160). The reflectance of samples was measured in wavelength range of 200 nm to 1100 nm using a UV-Visible spectrophotometer (Model Analytikjena SPECORD 250). In this research, five double-layer were coated and they are called for example G/Ag60/Al10, which, G is for glass substrate, Ag60 is first depositing thin film with 60 nm thickness and Al10 is second depositing thin film with 10 nm thickness.

3. Statistical Analysis

The statistical characteristics can be described with the height-height correlation function H(r),

$$H(r)\big|_{r=md} = \frac{1}{N(N-m)} \sum_{j=1}^{N} \sum_{i=1}^{N-m} \left[h(i+m, j) - h(i, j)\right]^2 \tag{1}$$

Where $m = 0,1,2,\cdots,N-1$, and d is the horizontal distance between two adjacent pixels, and $h(i, j)$ is the height of the surface measured by AFM at the point (i, j) for $N \times N$ total number of points . The average height overall surface points $\langle h \rangle$, and the interface width w (or rms) value of the surface roughness can be expressed as [17]:

$$\langle h \rangle = \frac{1}{N} \sum_{i,j=1}^{N} h(i, j), \tag{2}$$

$$w = \frac{1}{N} \sqrt{\sum_{i,j=1}^{N} \left[h(i, j) - \langle h \rangle\right]^2}\,. \tag{3}$$

Far from the equilibrium state, for self-affine surfaces, the dynamic scaling hypothesis suggests that the height–height correlation function has a power-law behavior [18],

$$H(r) = w^2 \begin{cases} (r/l_0)^{2\alpha} & r << l_0 \\ 2 & r >> l_0 \end{cases} \tag{4}$$

Where α is the roughness exponent that describes local "wiggly" of the surface (or degree of the random fluctuation in the short range) and l0 is the lateral correlation length (the largest distance which the height is still correlated). The roughness exponent α is directly related to the fractal dimension Df of the random surface by Df = E + 1 – α with 0 < α < 1, where E + 1 is the dimension of the embedded space (E = 1 for a profile; E = 2 for a plan).A larger value of α correspond to a locally smooth surface structure while a smaller one corresponds to more locally jagged morphology [18]. The statistical analysis of AFM data was done using the height distribution histograms. The height asymmetry is described by the statistical parameters such as surface skewness and kurtosis. In statistics, skewness and kurtosis are a measure of the asymmetry and the peakedness of the probability distribution function of a random variable, respectively. These two parameters represent the shape of the surface height distribution and can be defined as [17],

$$R_{sk} = \frac{1}{w^3} \sum_{i,j=1}^{N} \left[h(i,j) - \langle h \rangle \right]^3, \tag{5}$$

$$R_{ku} = \frac{1}{w^4} \sum_{i,j=1}^{N} \left[h(i,j) - \langle h \rangle \right]^4. \tag{6}$$

For comparison of these parameters for all samples, we have used a sufficiently large number of independent random variables with a normal distribution [19].

4. Results and Discussions

In order to study the effects of coating a very thin film of Al and Cu (10 nm) on Ag film and for opposite case of deposition on the surface morphology and the optical properties of these thin films, five samples with the experimental conditions which are presented in table 1 were produced, (i is discharge current, V is the plasma voltage, P is the electrical power and R is the deposition rate).

Table 1: Coating condition of metallic nano layers.

Sample	i (A)	V (V)	P (W)	R (nm/sec)
Ag	0.2	10±300	1±60	0.05±2
Al	0.4	10±330	1±132	0.05±0.8
Cu	0.4	10±350	1±140	0.05±0.8

4.1 Investigation of the Statistical surface morphology

Fig 1(a-e) shows SEM images of the produced samples which were deposited on glass substrate.

As shown in figure 1(a-e) one can observe that coating of a very thin layer of aluminum and copper on or under of Ag film causes suppress or lessen the agglomeration of Ag film. Figures 2 (a-e) shows the 3-dimensional AFM images of the Ag film, Ag/Cu and Ag/Al double-layers.

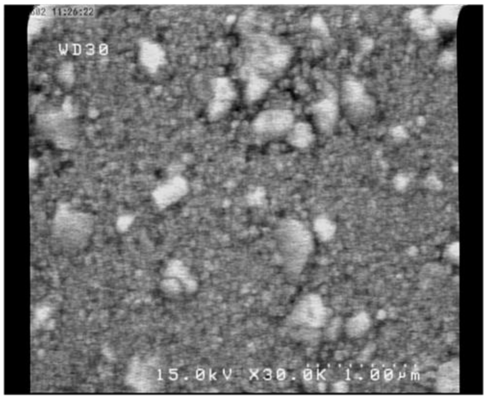

Fig 1-a: sample G/Ag60

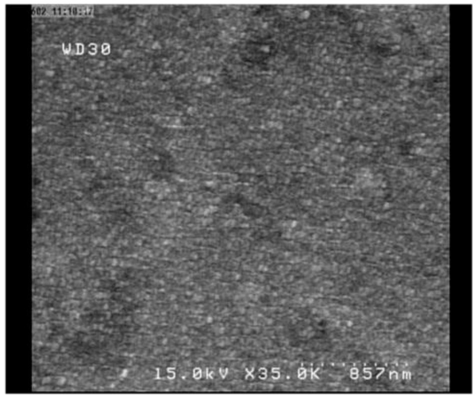

Fig 1-b: sample G/Al10/Ag60

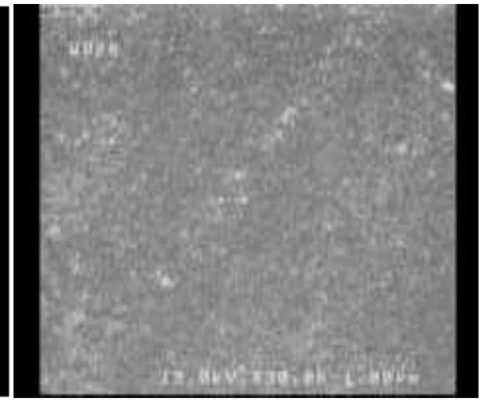

Fig 1-c: sample G/Cu20/Ag60

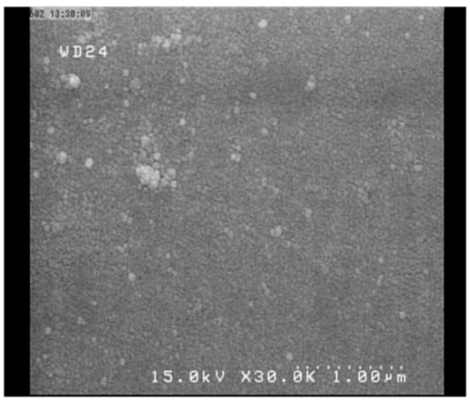

Fig 1-d: sample G/Ag60/Al10

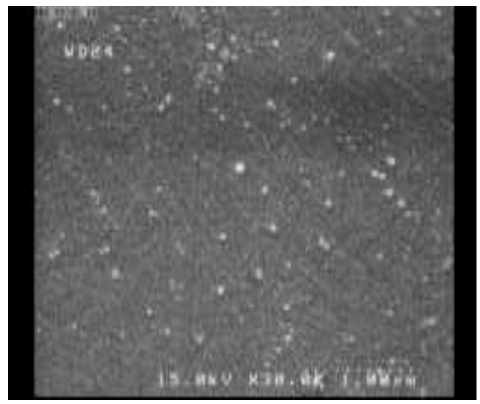

Fig 1-e: sample G/Ag60/Cu10

Figure 1: Two dimensional SEM images of all samples.

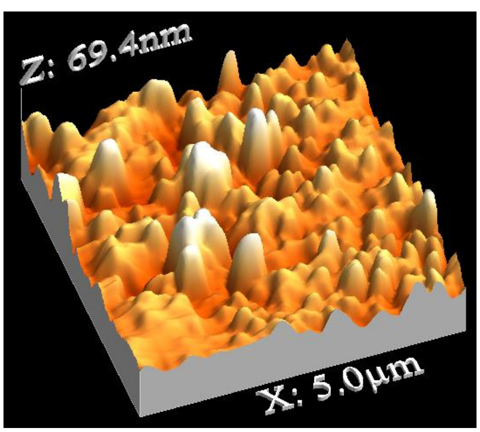

Fig 1-a: sample G/Ag60

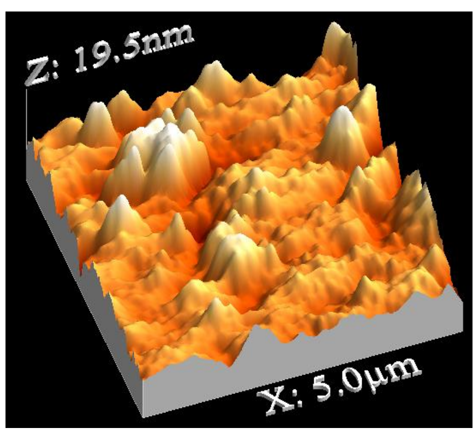

Fig 1-b: sample G/Al10/Ag60

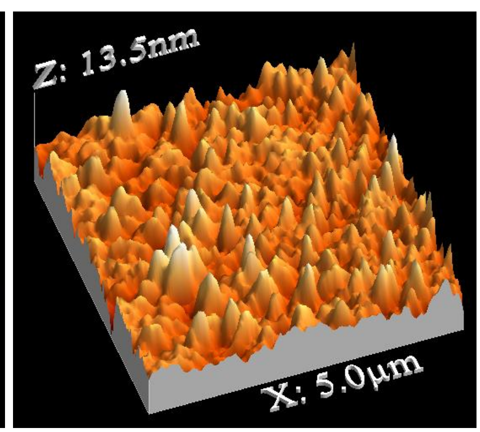

Fig 1-c: sample G/Cu20/Ag60

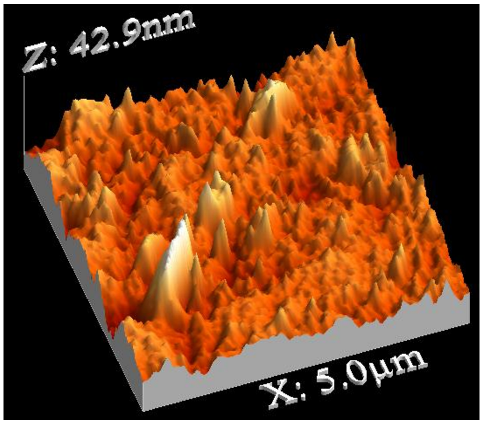

Fig 1-d: sample G/Ag60/Al10

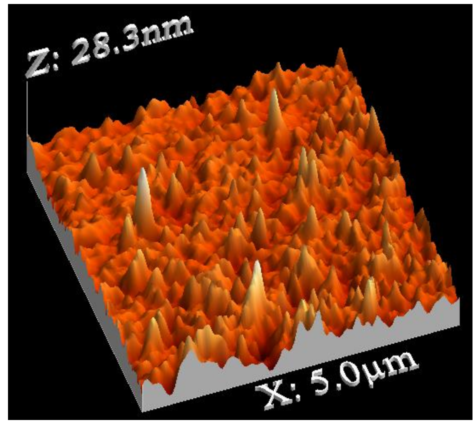

Fig 1-e: sample G/Ag60/Cu10

Figure 2: Three dimensional AFM surface images of all samples

As is apparent from figures 2(a-e) when there is a thin layer (10 nm) of aluminum or copper below or on the silver film, the surface roughness is reduced (As was seen in the SEM pictures). Calculating the RMS surface roughness with equation (3) for all of the samples, Ag thin film has maximum value (8.65 nm). This represents an increase in the height fluctuations than the average height. The one-dimensional cross-section scans of surface profiles for all of the samples are also plotted in figure3.

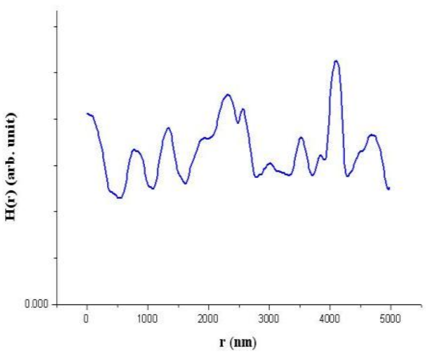

Fig 1-a: sample G/Ag60

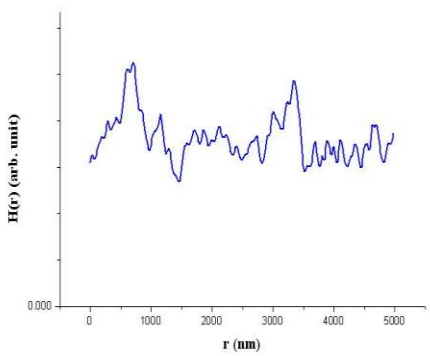

Fig 1-b: sample G/Al10/Ag60

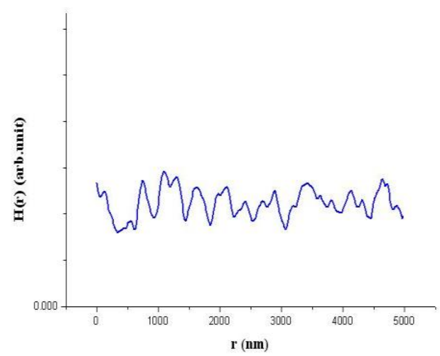

Fig 1-c: sample G/Cu20/Ag60

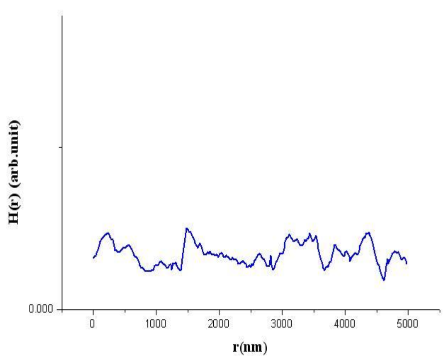

Fig 1-d: sample G/Ag60/Al10

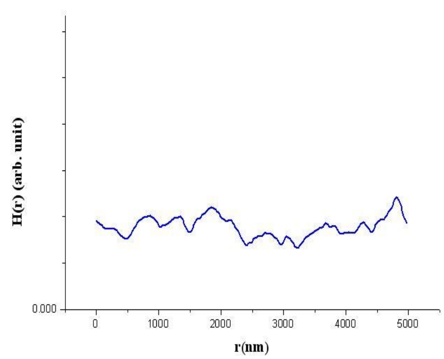

Fig 1-e: sample G/Ag60/Cu10

Figure 3: One-dimentsional AFM surface profile scans of thin films.

For obtaining the correlation length, height-height correlation function was calculated with equation (1). Figure 4 shows the height-height correlation function as a function of position *r* for Ag thin film.

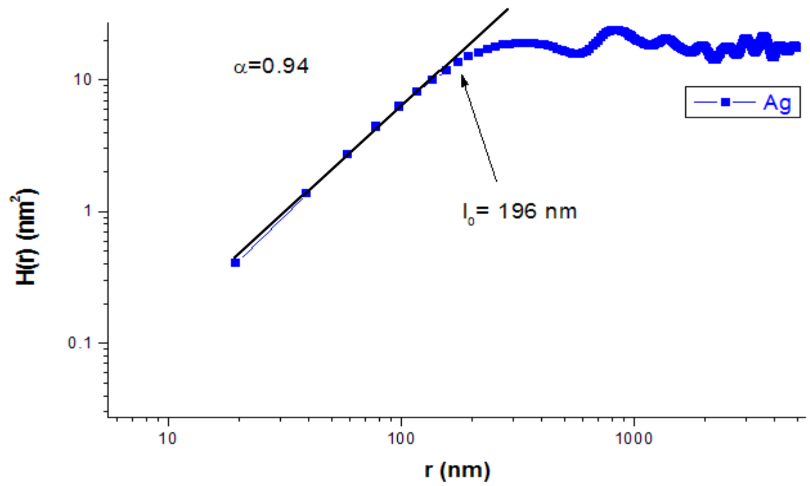

Figure 4. Height-height correlation for Ag thin film versus position *r*.

The slope of the curve at small scales yields the roughness exponent (2α) of the corresponding surface. The correlation length achieved by the height–height correlation function is represented in figure 5, for all samples.

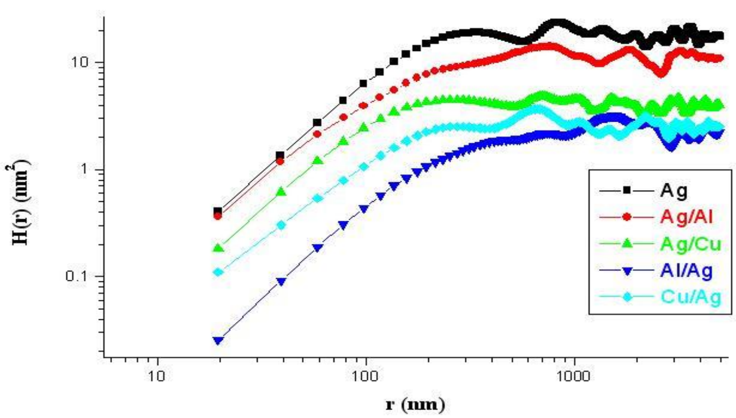

Figure 5: Height-height correlation function for all of the samples versus position *r*.

The saturation limit in these curves is the correlation length which is the lateral size of the grains. The values of the RMS roughness, mean height, correlation length and roughness exponent (α) are summarized in table 2.

Table 2: Statistical parameters which obtained for all of the samples.

Samples	Correlation length (nm)	RMS (nm)	Avg Height (nm)	D_f
G/Ag60	196±15	8.65±1	33.9±1	2.06
G/Ag60/Cu10	78±15	2.35±1	8.35±1	2.06
G/Ag60/Al10	157±15	3.99±1	17.02±1	2.3
G/Cu10/Ag60	78±15	1.59±1	7.08±1	2.49
G/Al10/Ag60	196±15	2.35±1	9.11±1	2.15

Deposition of Cu under and on Ag film reduced the correlation length, while when Al was used the correlation length remained unchanged, specially when Al was the first coating layer. But the surface roughness and average height showed reduction when a very thin film of Al and Cu was coated under and on Ag film. The height asymmetry is described by the surface statistical parameters such as skewness and kurtosis. These parameters are calculated by equations (5) and (6), respectively. Figure 6 gives the height distribution histograms for samples that acquire from AFM analysis, which are normalized using the central limit theorem [19].

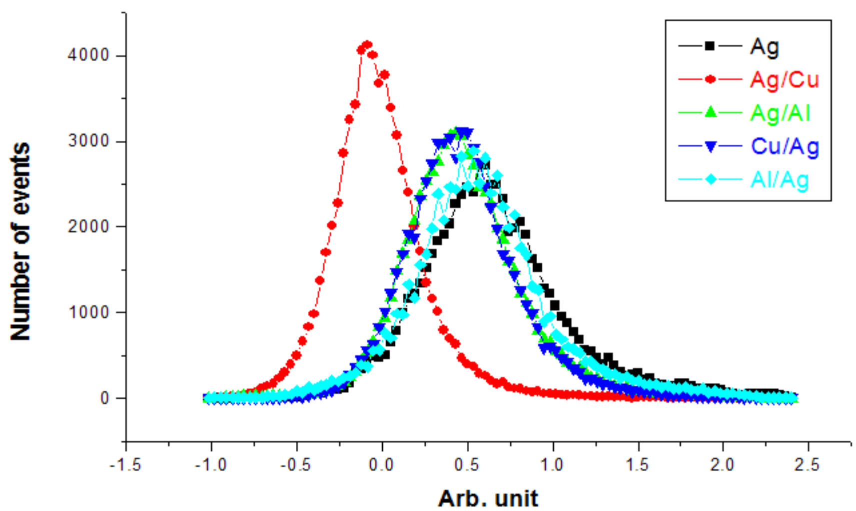

Figure 6: Height distribution histograms from AFM analysis for all samples.

Table 3 shows the values of the skewness and kurtosis for all samples. All samples have positive skewness, which means the number that valleys are more than the number of heights. Kurtosis which shows the peakedness of the probability distribution function and have positive values for all samples, film surfaces with positive skewness (more than 0.2) and high kurtosis values (larger than 3) are favorable for tribological applications (low friction surfaces) [20].

Table 3: Skewness and kurtosis for sampels.

Samples	Skewness	Kurtosis
G/Ag60	0.69±0.01	4.36±0.1
G/Ag60/Cu10	1.13±0.01	7.67±0.1
G/Ag60/Al10	0.56±0.01	4.87±0.1
G/Cu10/Ag60	0.7±0.01	4.74±0.1
G/Al10/Ag60	0.54±0.01	4.52±0.1

These results are roughly the same except for sample G/Ag60/Cu10, these high values of skewness and kurtosis produce sharp profile in height distribution function (Fig 6).

4.2 Investigation of The reflectance of thin double-layers

Figure 7 (a,b) shows the reflectance (*R*) as a function of wavelength for Ag thin films (10, 60, 90 nm).

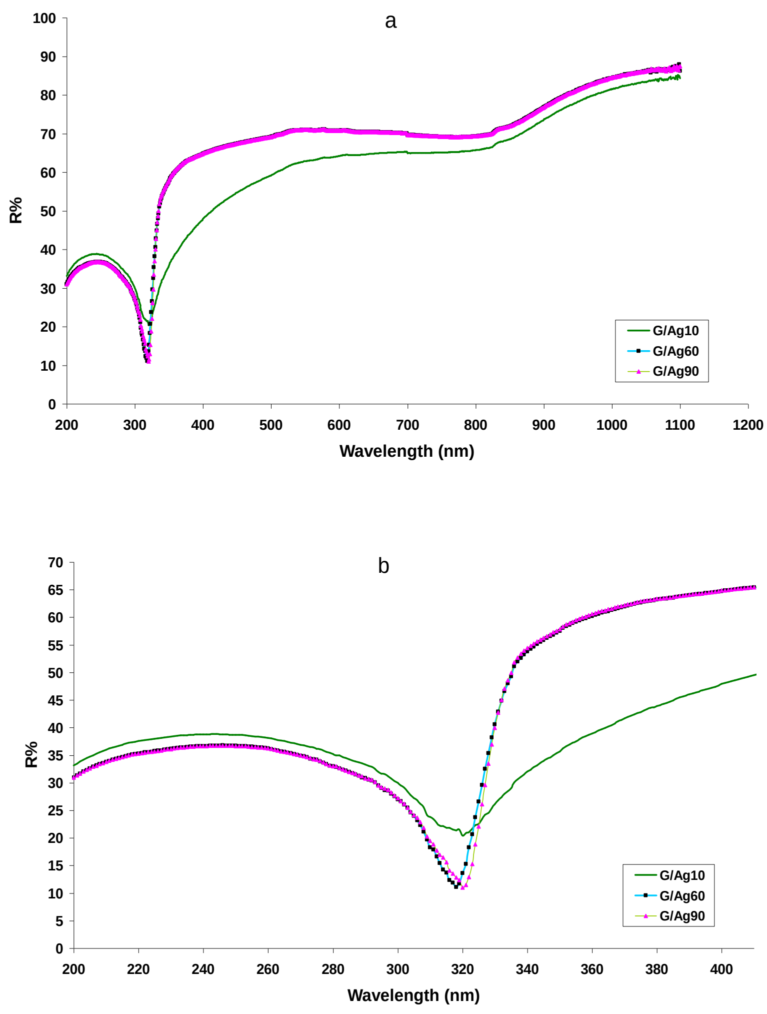

Figure 7(a,b): Shows changes of reflection power (R) of Ag thin layers.

As it can be seen in figure 7, the increase of thickness can increase the reflectance, but graphs of R against λ for 60, 90 nm Ag thin film are on top of each other, which means after certain amount of film thickness, the reflectance remain constant except near 320 nm range. There is a minimum reflectance (almost 10% at near 320 nm range) due to a surface plasmon [11]. The minimum reflectance is very important for SPR measurements, but in other metals this minimum is not as sharp as for Ag thin films. As Ag film thickness increases the minimum peak of the reflectance show reduction from 21% to 11% and also shifts toward lower wavelength (316 nm) , this can be due to variation of grain size of Ag. Comparison of the reflection power (*R*) of Ag/Al thin double-layers and Ag thin film is shown in figure 8, 9 (a,b).

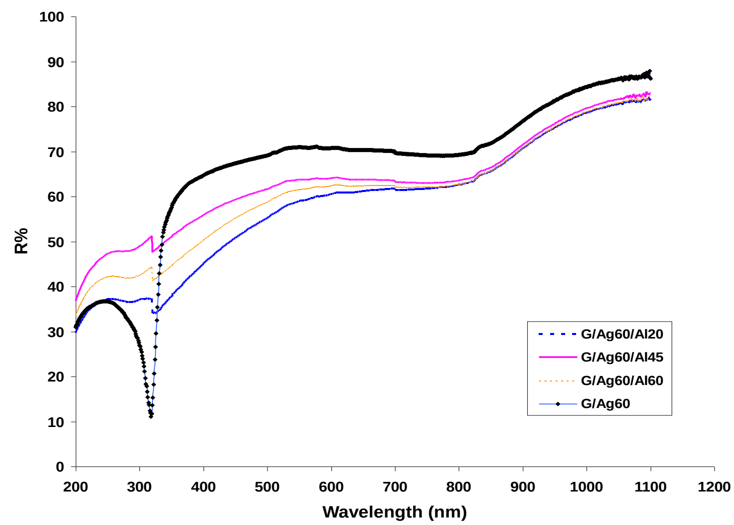

Figure 8: Shows changes of reflection power (R) of G/Ag/Al thin double-layers

From the figure 8, it was found that the deposition of a very thin film (20, 45, 60 nm) of Al on Ag thin film (60nm) varys the optical properties and Ag minimum peak drastically, the minimum sharp peak of Ag disappeared in G/Ag/Al films and this double-layers showed the same behavior of the reflectance as pure Al film.

Also the deposition of Al (10-60 nm) under Ag (60nm) film (G/Al/Ag) changes the reflectance in wavelength range of 200-500 nm, (Fig 9 (a, b)) and this double-layer showed the same behavior of as pure Ag film with this difference that the minimum peak position was shifted and the reflectance was decreased. These can be due to different behavior of dielectric function of Al and Ag, or the various number of valance electrons of Al and Ag, either may be due to interference of light in a layer of aluminum – Ag. Figures 10, 11(a,b) show the reflectance (*R*) of Ag/Cu thin double-layers and Ag thin film.

As can be seen in figure 10, with deposition of copper thin film (10 nm) on a thin film of silver (15-90 nm), minimum reflection of silver (at 320 nm) disappears. The variation of the reflectance against wavelength for these double-layers (G/Ag/Cu) is very similar to behavior of the single copper thin films.

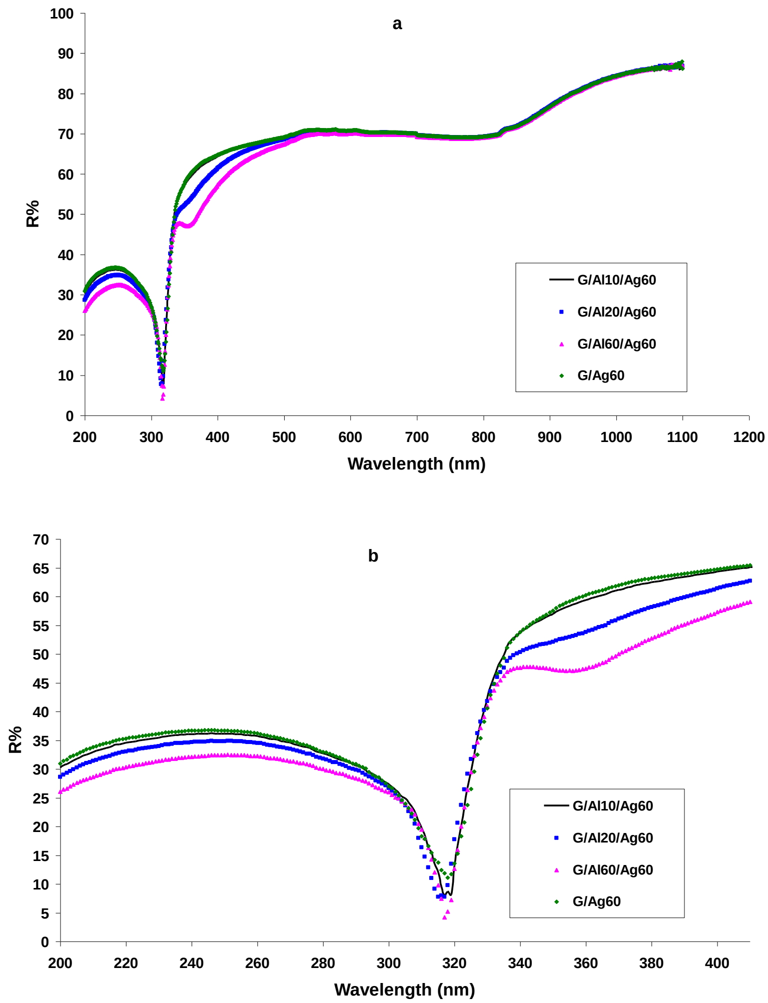

Figure 9 (a,b): Shows changes of reflection power (R) of G/Al/Ag thin double-layers.

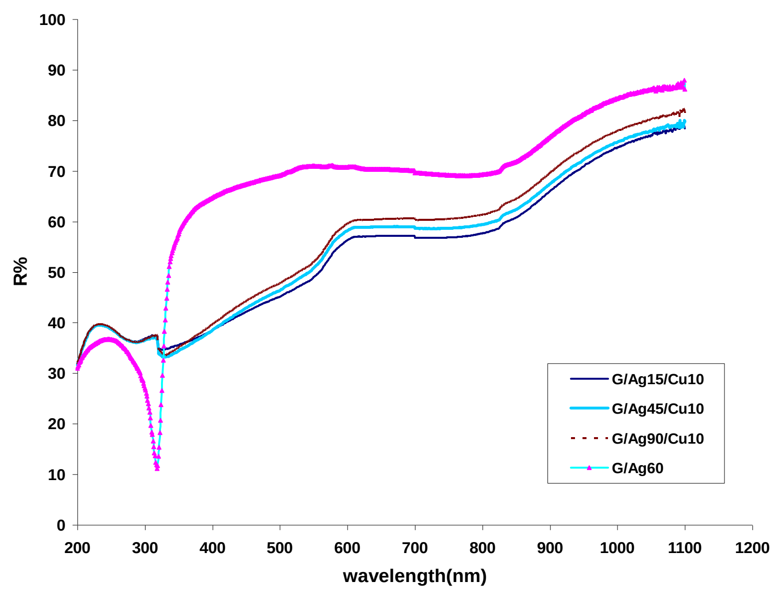

Figure 10: Changes of Reflection power (R) of G/Ag/Cu thin double-layers

As can be seen in figure 10, with deposition of copper thin film (10 nm) on a thin film of silver (15-90 nm), minimum reflection of silver (at 320 nm) disappears. The variation of the reflectance against wavelength for these double-layers (G/Ag/Cu) is very similar to behavior of the single copper thin films.

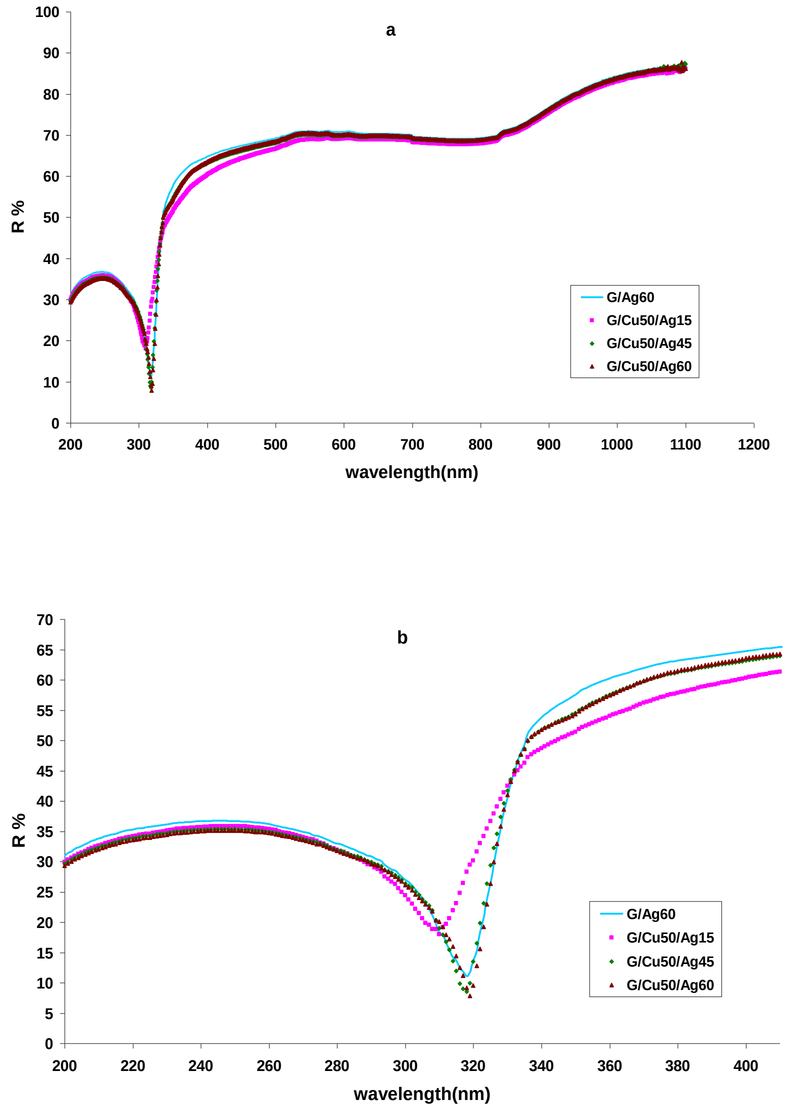

Figure 11: Changes of Reflection power (R) of G/Cu/Ag thin double-layers.

The behavior of the reflection power of G/Cu(50nm)/Ag(15, 45, 60 nm) with wavelength are similar to reflection of a single layer of silver, with this difference that the minimum peak position was shifted to higher wavelength and the minimum reflection peak value was decreased. This result is very interesting, because the copper layer in the wavelength range near 320 nm has relatively high reflectivity, but in a double layer of copper – silver the reflectance is reduced. One of the characteristics of copper is relatively good adhesion on glass (better than silver), these results show that if Cu is used as first layer for Ag coating in low wavelength (λ <350 nm) sharper minimum peak of the reflectance can be obtained while for higher wavelengths (λ>450 nm) reflectivity is the same as single Ag film.

5. Conclusion

Deposition of Al and Cu on Ag film and as its substrate vary the optical and structural properties , as well as its surface roughness.When there is a thin layer (10 nm) of aluminum or copper below or on the silver layer, the surface roughness is reduced and agglomeration of Ag film suppress or lessen. Deposition of Al and Cu under Ag film increased correlation length and on Ag thin film decreased it. All samples have positive skewness, that means more number of valleys than number of heights. Kurtosis and skewness for G/Ag60/Cu10 has maximum value. Higher Ag film thickness produces deeper peak of the reflectance minimum at 320 nm. When Al and Cu thin film (10 nm) were coated on Ag films the reflectance variation against wavelength were similar to Al and Cu single thin films and minimum peak of reflectivity of Ag was disappeared, but when Ag thin film was deposited on Al and Cu films the minimum peak was shifted and showed reduction. This is very important for SPR studies and gaining better ahision of Ag to glass substrates.

Acknowledgement

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