Copper Thin Film Deposited By PVD on Aluminum AA4015 Substrate for Thermal Solar Application

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Abstract. The copper nanoparticles (CuNP) films have been deposited on Aluminum-4015 substrate by PVD technique. Structural of thin film layer achieved have been analyzed by X-ray diffraction (XRD). While the chemical composition percentage of the multilayers (Zn-Ni) combined with thin layer and substrate evaluated via ED-XRF, other characterization likes surface morphology have been investigated by using scanning electron microscopy (SEM), FESM and AFM. Optical properties especially thermal absorption was measured in the UV/Vis range. The effect of coating parameter like time coating resulting different thickness thin film (50,100 and 150) nm deposited on Aluminum substrate have been studied and the influence on optical properties. SEM analysis and AFM results show that prepared films were denser with nanosize grains between (26-54) nm. Also, XRD results show nano copper was the main chemical component in the films. The films prepared by this technique have better optical properties like good absorption ranged between (87%-97%). Decreasing the emittance and increase the absorption leads finally achieve a good selectivity coating using in the solar thermal application.

1. Introduction
The sun is one of the most important natural sources of energy because clean, cheap and free of toxic emissions also can be converted to alternative sources [1, 2]. The solar absorber is the central part of a solar thermal collector, and its function to collects the sunlight energy then alters this energy into a more usable or storable energy form converting to heat [3].

The absorber surface used in thermal solar collectors requires high absorption in the UV. Vis. Range solar spectrum and a low thermal emissivity in the NIR rang solar spectrum [2, 4]. Several techniques, based on different absorption mechanisms including light trapping, particulate coatings such as vacuum techniques, electroplating, EPD, and sol-gel are currently used to produce solar absorber surfaces [3, 5, 6]. Electroplating is one of the most common methods of selective coating achievement because it is a simple and controlled method as well as cost effective [7, 8]. Bright Nickel electroplating is used in absorber surface due it is effective in thermal stability and prevents diffusion between thin layer of nanoparticles and base metal acting as inter layer between thin film and the metal surface in addition to good surface finish obtained [9,10].

Nanomaterial with unique properties that are completely different from the bulk had crystal scale size ranging from one to one hundred nanometers have been attracted researchers in many fields [11]. Copper nanoparticles (CuNP) are very attractive due to their physical and thermal properties such as high thermal conductivity [12]. Cu NP also have high surface area to volume ratio, low production cost, antibacterial potency, catalytic activity, optical and magnetic properties as compared to other metals [13,14]. Many researchers have fabricated absorber surfaces using solar energy applications [15]. Recently, researchers have proposed using nanotechnology in the field of solar selective coatings.
to improve the efficiency of the absorber surface in the solar thermal collector thus improving the performance in the solar thermal application [16]. Improving the performance and increasing the efficiency of solar thermal absorbers require enhancement of the optical characteristics of solar coating absorbers and making them thermally stable at high temperatures. Z.A.A. Majid et al., (2016), [17], investigated the Aluminum AA6063 coated with black paint and comparison with uncoated base metal results show increases in optical properties due to black paint. Ervin Šesta et al. (2018), [18], proposed that nanoparticles of graphene could be modified by sol-gel method, these nanoparticles using spin coating deposited onto the aluminum substrate via spin coating technique with thickness range 1 μm±0.1. This modifies nanoparticles of graphene didn’t effect on optical properties in another side good important in corrosion inhibition with the addition of critical value (≈ 0.05 wt. %) The importance of this type of coating in addition to possessing optical properties has high resistance to corrosion.

This study aimed to prepare efficient thin film nanostructured (CuNP) with good optical properties and thermal stability using in the solar energy field. This thin film working as solar selective absorber coating gathered with two layers zinc and Nickel deposited on Aluminum metal substrate utilization thermal evaporation technique.

2. Experimental

2.1 Substrate

In order to reduce the cost of materials to the minimum and improve efficiency, the recommended materials to build solar absorber was Aluminum, the chemical composition of aluminum presented in Table 1 have been investigated via spectrometer (OES) type (Foundry-Master xpert) S.N 52Q0089 Germany. Microstructure also analyzed by using the optical microscope type KRUS Company model MBL.3300, Germany as revealed in Figure 1. This substrate was chosen due to good thermal conductivity, lightness and corrosion resistance, wherever it represented the next best readily available conductor for the sheet was Aluminum whose conductivity not as good as that of copper, is still quite good[ 19,20].

| Element | Al  | Si  | Fe  | Cu  | S   | Mn  | Mg  | Ti  | V   | Zn  | Ni  | Ca  |
|---------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Composition | 97.531 | 2.313 | 0.099 | 0.004 | 0.015 | 0.001 | 0.059 | 0.005 | 0.004 | 0.001 | 0.005 |

Figure 1. show the microstructure of Al used in this study.
2.2 Preparation of Substrate

rectangular shape of Aluminum substrates pieces have been cut with dimensional (20mm×200mm×3mm) using band saw machine type Knuth Germany, and in order to hang the samples in an electroplating bath it should have a drill about (5mm) as in Figure 2 which it revealed the geometry of these samples.

![Figure 2. Aluminum substrate shape after cutting.](image)

2.3 Electroplating

2.3.1 Surface Preparation

Selection nickel electroplating is a good choice for its advantages in absorber surfaces due to thermal properties at high temperature with good stability, and its works as inter layer that prevents nanoparticles from diffusion between the surface of the base metal and thin film as well as good appearance and high finishing[21].

Before process of electroplating carried out some stages should have been taken into consideration in order to obtain good deposited layer of nickel including electropolishing, ultrasonic cleaning and alkaline, acid clearing as presented in Figure 3 below. This type of aluminum is manufactured with a thick protecting layer of alumina that has to be removed before it is ready for use as employ in process illustrated in Figure 3.
2.3.2 Zincate
The electroless process of metals and alloys is based on the deposition and reduction of metallic ions (reducing agents are formaldehyde, hydrazine, and hydroxylamine) from a solution to a surface without applying an electrical potential hence electrochemical reaction is the basic rule of electroless plating [22].

Zincate is a common type of electroless process that is carried out by the immerse aluminum substrate in an alkaline solution of zinc at 35 °C and times of immersion ranging from 5 seconds to 45 seconds. The time required to achieve a single zincate for this study the immersion time was 15 seconds with the stirring of the aluminum in the alkaline solution of zinc, to be followed by a rinse and clean in distilling water. The layer obtained with light grey color then aluminum will be able to be coated with nickel for application in thermal solar collectors, utilization suitable bath formations after zincate coating was carried out.

2.3.3 Bright Nickel
Electroplating is one of the conventional methods that have been used into a solar selective coating due to simple, easy to control, environmentally friendly and it is low in material consumption. The
solar thermal absorber based on nickel electroplating mechanism has been proposed due to high mechanical properties, long life product, intermediate layer utilization and stability at high temperature as well [23]. Mainly this process includes the chemical reaction between the metal coatings on the substrate alloy but is entirely dependent on the adhesion of the coating layer on the substrate alloy surface [24]. Nickel deposition achieved using Watts bath, the parameters and conditions related to nickel electroplating was revealed in Table 2. The layer obtained was shiny and had a good finish and ready for a thin film of nano copper.

### Table 2. bright nickel electroplating parameters

| Electroplating Conditions | Standard Parameters | Actual parameters |
|---------------------------|---------------------|-------------------|
| Temperature of electroplating | 50 - 60 °C | 53 °C |
| pH | 3.5 - 5 | 4.8 |
| Size of bath | - | 25 liters |
| samples size | - | (20 x 2)cm |
| Electroplating time | Max. 30 min. | 2 min. |
| Area of anodes to cathode | 2 :1 | 2(25 x25 x3cm) |
| The cathodic current efficiencies CCE | high | |
| baths Nickel type | Watts bath | Commercial watts baths |
| cathode and Anode distance | Minimum 2.5 cm. | 25 cm |

so as to employ substrate the specimen in vacuum chamber system of thermal evaporation specimen should prepared and catted to suitable size first of all the substrate cut like rectangular with dimensional (20mm×20mm×3mm) using band saw machine.

### 2.4 Nanomaterial Raw.

A copper nanoparticle was synthesized by Nanjing Nanotechnology Co. Ltd. CuNP powder was received with data sheet present with mean particles size of 24 nm. Table 3 gave the general specifications of CuNP as received.

### Table 3. illustrated specifications of CuNP.

| Property | Average Particle Diameter | Purity | Bulk Density | True Density | Color |
|----------|---------------------------|--------|--------------|--------------|-------|
| Value Units | 24 | 99.98 | 0.46 | 8.96 | Black |
| | nm | % | g/cm³ | g/cm³ | - |

### 2.5 Thin Film Procedure With Thermal Evaporation.

Thermal evaporation is one of the most practical methods to prepare thin film in order to use in as solar absorber in energy field [25]. Copper nanoparticles were deposited on Al substrate and Al platted Zn-Ni with dimensions (20mm×20mm×3 mm) using thermal evaporation which type of physical vapor deposition system that has been display in Figure 5. Cooling system must be operated firstly then vacuum chamber was pumped down to a base pressure of 2.5×10⁻⁴ Pa. Before putting the substrates into the vacuum chamber the coating material were prepared into the boat made from Molybdenum, starting turn on the heating the boat in the vacuum chamber knowing that system already turn on cooling and getting a good vacuum pressure till reaching the desirable pressure (1.1×10⁻⁴ to 2.7×10⁻⁵).as presented on table 4 then coating material have been evaporated slowly in order to get uniform deposition rate. The thin film obtains colored varied from reddish coppery to shiny blue azure as appeared in Figure 6.
Table 4. evaporation and melting temperatures of CuNP.

| Metal          | Density Bulk g/cm3 | Melting Temperature °C | Vapor pressure mbar. |
|---------------|--------------------|------------------------|----------------------|
| Copper (Cu)   | 0.46               | 1083                   | 1.1-2.7 3-3.7        |

Figure 4. Thermal evaporation unit using in study.

Figure 5. Photo images representing the appearance of coated samples (a) Al-Zn-Ni (b) Al-CuNP (c) Al-Zn-Ni-CuNP. (d) Si- CuNP. (e) glass- CuNP.

3. Results and Discussion

3.1. Thickness

Thin film thickness measured via Ellipsometer /black comin3 t /20cr instruments. This method is based on interference of the light beam which was reflected from thin film surface and substrate bottom, with the error rate at 3%. Three different thicknesses of coating (CuNP) were deposited over Al by increasing the coating time (2, 4 and 6) minute, while keeping an applied pressure vacuum range between (1.1×10⁻⁴ to 2.7×10⁻⁵) Figure (7) present the thin film thickness obtained by coating time 4 min. The Figure shows thickness approximates (990 A0) angstroms which is equivalent to (99 nm) nanometers. The CuNP coating thickness increases from sample C1 to C3 as demonstrated in figure 7. Thickness coating affected on particles size and roughness while optical properties alter by thickness dramatically.
3.2. XRD pattern

The X-ray diffraction test is important evidence to prove the presence of phases as well as the appearance of some structures at the nanoscale, besides, the other phases found in the multi-layers that deposited on the Al the base metal. On the other hand, the presence or absence of a phase depends on the thickness of the layer in addition to the depth of the x-ray penetration. The XRD results of CuNP thin films achieved with multi layers Zinc-nickel was present in Figure 8 have been achieved using Shimadzu, model 6000 while scan of speed 5.0 degree for a minute and diffraction angle between 20-80. The X-ray results were arranged so that the criteria were the peak position and the sequence from the bottom toward the top. A bottom pattern was the Al as received followed by Al electroplated with Zn-Ni, the final pattern represented the Al coated with Zn, Ni, and CuNP respectively. Black lines revealed variety peaks with values of 38.5566°, 44.8097°, 65.1789° and 78.3102° matched with Aluminum substrate with (111), (200), (220) and (311) respectively(Ref.#pdf00-004-0787). While diagram green colored exhibited peaks at 44.3879, 51.4795, 65.133 and 77.9972 referred to Nickel with structure (011),(200),(220) and (103) (Ref. # pdf00-004-0850 and #pdf00-045-1027).lastly the red lines diagram show peaks indicted the 38.4640 belong to Zinc with structure (100) (Ref.pdf#00-004-0831), other peaks like 44.1000o refer to CuNP (#pdf00-001-1241).

3.3. Energy Dispersive X-ray Spectroscopy (ED-XRF)

Ed-XRF test was adopted as a robust test showing as present evidence of metals and their percentage, Thin film solar selective coating combined with multi layers (Ni and Zn) deposited on Al substrates has been analyzed, calculating the composition of thin films with micro multi layers investigated quantitatively and qualitatively. Figure 8 elucidates the chemical composition percentage for specimen belongs to the system (Al /Zn-Ni- CuNP), as in Figure 9b. This evaluation of chemical composition.
percentage of the thin layer of CuNP combined with aluminum substrate carried out using EDX-7000 type Shimadzu Company, Japan.

Figure 8. ED-XRF analysis of (a) CuNP and (b) Zn-Ni deposited on Al.

The energy of fluorescent recognizes the elements Al, Zn, Ni, and CuNP while in another side the intensity of this energy is a measure of the element's concentration. Hence the high intensity elements should have a high concentration in the composition. It was observed that the dominant phase was aluminum with the highest percentage for being the base metal, while nickel and zinc was the second level as a microlayer with thickness ranged between 3-3.5µm, lastly, the lowest percentage was indicated for CuNP thin film.

3.4. AFM

Studying the features and characteristics of the thin film surface of copper is an important influence on the efficiency of solar thermal absorber. On this basis topography and asperities of surfaces Copper nanoparticles (CuNP) have been studies by using an atomic force microscope (AFM) type Nano compact AFM manufactured by PHYWE German Co. AFM gave statistical values for grain size, how to distribute it on surfaces and the roughness of the thin film surface.

It is observed that roughness affected on absorption, hence to achieve absorption surface roughness necessary [26, 27]. The Figure 10 represent the surface topography of the nano-copper deposited on the aluminum directly as in figure 10a that appear as surface of hillocks, while presence of zinc and nickel in the Figure 10b recognized that the nanograins tend to semi pyramid shape and this corresponds to the fact that this surface texture being as harvesters or trapper sunlight, via multiple reflections mechanism of selective solar coating (SSC), that lead to improving optical properties especially absorption [28]. While semi pyramids shape was clearly recognized in figure 10c, belong to the copper nanoparticles deposited on the glass.
Figure 9. Display the 3D image of nanocopper topography (a) CuNP-Al, (b) CuNP-Zn-Ni-AL and (c) CuNP-glass.

It’s clear that the nanoscale of grain size belongs to copper thin film ranging from 26 to 54 nm as shown in the table 5, which reveals that the dominant grain size was 54 nm.

Table 5. Show the grain size distribution of CuNP thin film

| Avg. Diameter: 39.63 nm | <=50% Diameter: 26.00 nm |
|------------------------|--------------------------|
| Diameter (nm) | Volume (%) | Cumulation (%) | Diameter (nm) | Volume (%) | Cumulation (%) |
| <=10% | <=50% | <=90% | <=10% | <=50% | <=90% |
|------------------------|--------------------------|
| 26.00 | 0.35 | 0.35 | 40.00 | 6.11 | 54.95 | 54.00 | 3.75 | 89.99 |
| 28.00 | 10.36 | 10.71 | 42.00 | 6.61 | 61.56 | 56.00 | 3.60 | 93.59 |
| 30.00 | 8.75 | 19.47 | 44.00 | 5.21 | 66.77 | 58.00 | 3.40 | 97.00 |
| 32.00 | 7.46 | 26.93 | 46.00 | 6.11 | 72.87 | 60.00 | 2.50 | 99.50 |
| 34.00 | 8.61 | 35.54 | 48.00 | 5.51 | 78.38 | 62.00 | 0.50 | 100.00 |
| 36.00 | 7.46 | 42.99 | 50.00 | 4.30 | 82.68 | 82.00 |
| 38.00 | 5.86 | 48.85 | 52.00 | 3.55 | 86.24 | 86.00 |

3.5. SEM results

Scanning electron microscope images with a magnification force of (540x, 2700x and 27,000x) for Figure (10-a,10-b and 10-c) respectively that analysis of surface topography belongs to copper thin film prepaid by thermal evaporation which appears as dense layer of small, semi-spherical nanoparticles and distributed uniformly and over the sample surface area. Precise details of surface topography were investigated utilization Field Emission Scanning Electron Microscope (FESEM) as present in Figure 11c.

The effect of the presence of the nickel-zinc layer, which gave a good surface finish, resulted in the homogeneity and uniformity of the thin film layer of copper nanoparticles figure 11a as compared to the one directly coated on the aluminum Figure 11a.
3.6 Optical properties

Absorption is one of the most important physical properties, which is the first criterion of selective coating efficiency used in the solar thermal collector, tests have been carried out utilization UV-Spectrophotometer, model-1800, UK in wave length range between (300-1100) nm. The increase in absorbance in general as result of increasing the thickness of thin film, This due to increase the degree of crystallization by increasing the thickness this will lead to increase in the particle size in other hand this may obtain higher roughness cause efficient absorbance. The greater of absorbance proportional to the higher thickness of the thin films, as well as being agreement with relationship between thickness and absorption of prepared thin film. Increasing thickness of the thin film resulting increased absorptivity and this is what is called law Lambert in absorption [29]. Table 6 and Figure 13 shows a comparison between the behaviors of the absorption spectrum of copper nanoparticles as function to the thickness.

![Figure 11](image)

**Figure 11.** a comparison of the behavior of the spectral absorption spectra of CuNP thin film prepared with different thickness deposited on glass.

**Table 6.** presented the absorption values as function to the thickness

| No. of sample | Thickness(nm) | [α] %  |
|---------------|---------------|--------|
| C1            | 50            | 87.603 |
| C2            | 100           | 94.827 |
| C3            | 150           | 97.154 |

Prepared by different thickness, as the figure shows the added defect has worked on Increasing the absorption - and significantly - of the waves with low photonic energies, especially those at the end the
visible and infrared regions are nearby, and this is due to the intensity of the localized levels formed by the atoms.

4. Conclusions
Regarding to the results obtained nanocopper particles (CuNP) exhibited good physical properties that was demonstrated through the values of absorption (97.154%), While nickel layer combined with Zinc is considered an excellent option to avoid the problems of diffusional the nanoparticles to the base metal and obtain a good thermal stability and reducing the thermal emission, which improved the performance of the solar collector.

While the absorption values were a proportional increment to the thickness of the thin film from 87.603% to the highest value obtained 97.154%, which are desirable because absorptivity is the most important criterion in the performance of the absorbent surface of the solar thermal collector.

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