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A low-temperature gold coating of the dielectric surfaces employing phosphine gas as a reducing agent

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1. Introduction.

Gold dielectric coatings are widely used in industries. Gold coatings have various functions such as [1-3]: protection from corrosion; catalytical activity; bactericidal ability; high electrical and thermal conductivity, low and stable contact resistance over time; necessary requirements for solderability; the ability to reflect infrared rays; use for decoration.

Applications of gold coatings depend on physico-chemical properties of this metal.

Gold has a very high resistance to corrosion. Therefore, since ancient times used as a method of corrosion protection [4,5]. Although such a coating base metals (in this case, the underlayer) has disadvantages (coating softness, high potential at point corrosion), it is common due to the fact that increases the lifetime of various electronic devices.

As per electrical and thermal conductivity gold is second only to silver and copper, which resulted in the application of gold coatings in the chemical industry, electronics and instrumentation [6,7]. In Electronics gold is used to cover various kinds of contacts, gold with nickel underlayer allows multiple resolderings cycles and ensures solderability for 6 months [8].

Almost 100% of gold's ability to reflect infrared rays allows its use in the glass industry, for metal window panes of buildings [3.8].

Gold is also known for its catalytic properties. Gold catalysts have been used for the oxidation of alcohols, aldehydes and carbohydrates [9,10], therefore methods of applying gold particles at various carriers have been developed. For example, use of gold as a catalyst in automobile fuel system is promising [9]. Bactericidal activity of gold (Cu) is 2-3 times lower than silver (Ag), however, the bimetallic composition Ag / Au = 5 has the best bactericidal action, where a small addition of silver enhances the gold activity [11].

Requirements for gold coatings have led to the development of a number of gold-plating techniques. Conventionally, they can be divided into electrochemical (galvanic), chemical and physical methods. The most common method is a galvanic technique based on applying gold coating from the solutions on the basis of a complex salt, potassium dicyanoaurate(I),

$\text{KAu}(\text{CN})_2$ [4]. Electrolytes containing various additive elements, arsenic [12, 13], indium [14] and alkylsulfonic salts and acids [15] have been developed for gold coatings. The electroplating method allows also to obtain dense fine-grained semi-gloss bright gold coating containing dispersed diamond additives, which gives the coating high wear resistance, and retains increased electrical and technological properties [16]. The inclusion of ultrafine gold-silica gel or nanodiamond particles [5,8,17] on gold containing gel coating provides a nonporous, corrosion resistance, greater hardness and wear resistance as compared with coatings obtained using the method of precipitation tank.

The disadvantage of galvanic technique is the use of toxic cyanide compounds, the impossibility of coating on the inner surface and the need for pre-metallization. In chemical coating process cyanide, ferrocyanide, chloroauric electrolytes containing as reducing agents such as dimethylboran, hydrazine sulfate, sodium hypophosphite, citrate or tartaric acid [18,19] are used. Using chemical methods gold is deposited on copper, nickel and silver. When coating dielectric materials it is necessarily first to apply these metals to the surfaces.

One of the types of chemical plating is an immersion (contact) plating method [6,7,20,21]. This method is used for coating silver, copper and nickel. It provides quality coverage of complex parts or inner tubes cavities. The method has a limit on the coating thickness (less than 0.2 microns). Furthermore, when dielectric surfaces are employed, it requires a nickel precoating, which creates a multi-step process.

The physical gold coating methods [22-24] include vapor deposition, thermal evaporation based on organic compounds of gold and gold vapor condensation on the surface of a product or ion beam or laser sputtering of gold particles. The advantage of physical methods of coatings is the possibility of applying gold directly on the surface of the product, while the disadvantage is the need for expensive and complex installations.

From literature it is evident that there is still a need for low temperature gold coating methods using gaseous reducing agents. The basis of our proposed method is to use a gaseous phosphine

as a reducing agent. Earlier we employed this reducing agent for coating technologies on metal and dielectric materials such as copper-phosphorous and silver films [25-28].

The process, that is described in this paper, is based on obtaining gold coatings employing low temperature gaseous reaction between phosphine and gold chloride. Employing this gaseous reducing agent allows preparing porous coatings on dielectric materials and composite surfaces. Coatings are formed on both inner and outer surface of the treated material employing phosphine as a reducing agent. This helps increase of coating adhesion to fabrics and porous materials.

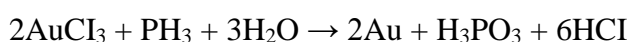
Use of water soluble reducing agents such as vitamin C has some difficulties associated with reduction inside pores of the dielectric materials, this can lead to creation of non-homogeneous coating. Use of other reducing agents such as gaseous hydrogen requires high temperatures and in this process it is not possible to use aqueous gold solutions.

Our described process is robust, easy to scale-up and to employ in industry for various applications. Since we did not target biomedical application of the coatings, toxicity is not an issue in our study. Moreover, in our work we employed a method that removes residues of unreacted phosphine.

In this paper, a low-temperature coating technique using gaseous phosphine is presented for coating of different surfaces. The obtained coatings were characterized employing electron microscopy, SEM techniques.

2. Materials and Methods.

A reaction of phosphine with gold chloride is outlined below. The special feature of this reaction is that the product of the reaction is pure gold without phosphides [29].



Separate stages of the gold coating process is shown in Figure 1.

To create a sorption layer it is necessary to create wettability of the surface of the product. For this purpose, preliminary procedures of etching and degreasing were carried out. We used the method recommended in the literature [18]. For nonmetallic materials, having a porosity or a rough surface, the etching step is optional.

Prepared samples (*Figure 1a*) were immersed in a gold chloride solution for 1-3 minutes. This produced a sorption layer (*Figure 1b*) on the sample surface.

It should be noted that the concentration of gold chloride in the solution used to create a sorptive layer affects the thickness of the resulting gold film. Thus at a concentration of 10 g/L to 150 g/L film thickness (for flat samples) changes from 0.03 microns to 0.5 microns.

The product was then dried at 25°C to create a wet film of gold chloride with sufficient permeability (*Figure 1c*). Drying time was generally 50-60 minutes. Thus the dried product was placed in a sealed chamber and fed to gaseous phosphine until its absorption termination. Our techniques for producing phosphine and its use to produce surface films, as well as the determination of film thickness did not differ from those given in [27,28].

As a result of the reaction of gold chlorine with phosphine a gold film was formed on the surface of the sample (*Figure 1d*), which still contained reaction byproducts. After washing with water we obtained a sample (*Figure 1e*) covered with a film of pure gold.

Gold coatings were created on the surface of cotton fabric and porous PVC materials. Samples were dipped for 3 minutes in a solution containing 100 g/L of gold chloride. Then by shaking the excess of gold chloride solution was removed. The sample was then dried at 25°C for one hour. The wet sample was placed in a sealed chamber where air was removed by purging with nitrogen. The camera was connected to a vessel with phosphine gas. The [27,30] equalizing vessels was filled with water, through which the vacuum created in the chamber, creating a flow of phosphine into the chamber.

In addition to change of the water level in the equalizing vessels can be judged on the speed of the process. Typically, the time spent for the reaction was 5-10 minutes. The sample was washed from byproducts and air dried. As it can be seen from *Figures 2a, 2b* a continuous characteristic gold yellow film was formed on the surface of the sample.

Au-Cu and Au-diamond coatings were prepared the following way. Preconditioning of the samples degreasing and etching operations were performed as described above. A surface layer of gold chloride solution was achieved through dipping the samples for 3–5 s in a gold chloride solution (200 g/l) followed by shaking to remove liquid excess. Spraying of diamond powder onto the surface sample was conducted with the device as described in [28]. To prevent any premature drying of the surface film of gold chloride solution, the spraying time did not exceed 20–30 s. The mass of the diamond powder sprayed was 1.6–1.9 mg/cm². In order to fix the particles of diamond powder onto the sample surface was treated by phosphine-containing gas as described in [28].

Characterization (structure and elemental composition) of the obtained coatings was performed using a scanning electron microscope (SEM), ISM-6490-LV (JEOL, Japan). Hardness measurements were performed using a coating hardness-2 Temp on samples of 50 mm thick lapped to a flat steel plate 500x500x10 mm by grease "litol." The hardness values were calculated as the mean of 5 measurements.

3. Results and Discussions.

Gold coatings of samples of different materials were shown in Figure 2.

Deposition of gold films was studied on samples of cotton fabric (*Figure 2a, Table 1*) and porous PVC (*Figure 2b, Table 2*). In *Figures 3-6* SEM images and EDX spectra of the obtained films were presented. At the same time due to the small thickness of the coating peaks of the elements constituting the base material appeared on the spectra. The percentage of these base material

elements varied according to the thickness of the gold film. When analyzing the composition of the obtained coating these base material peaks were not considered. Thus, when analyzing film on cotton fabric without considering spectra carbon, nitrogen and oxygen included in the original tissue, the film consisted of pure gold (*Figure 3, Table 3*).

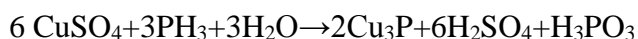
On a sample of a porous polyvinyl chloride, disregarding the elements included in the original polyvinyl chloride, the resulting coating also consisted of pure gold (*Figure 4, Table 4*). The darker regions in *Figure 4* corresponded to the pores.

Often, to improve hardness and wear resistance other metal additives are introduced into the gold, particularly copper. It is known [25, 26] that phosphine gas can reduce copper ions forming phosphide copper. That is why we studied a process of combined reduction of copper and gold ions by introducing copper chloride (II) in the solution of gold chloride. This reaction gave formation of copper phosphide which is in agreement with other work [26]. Employing this method a composite Au-Cu coating can be formed.

We have studied the process of combined recovery of gold and copper on a gauze tissue (Article AA010278 *Figure 2c*). A solution containing 100 g/L AuCl₃ and 20 g/L CuCl₂ was used to create a sorptive layer.

Elemental composition (*Figure 5, Table 5*) after the deduction of the elements included in the fabric (C, O, Si, Cl, Ca) showed that the obtained film contained also copper and phosphorus besides gold.

The formation of copper phosphide is shown in the reaction below:



The content of copper phosphide in the film was 16.7% (by weight).

Employing low temperature gaseous reducing agents allows formation of composite gold containing coatings by introducing solid particles. These particles are sprayed on the surface of sorptive layer containing gold chloride and after that it is fixed by metal gold forming by reduction reaction of phosphine gas. This technology does not require drying of a sorptive later

as water content is reduced in the layer. This method can be used for incorporation of any particles that have wetting properties. In this work we used this technology for formation of gold-diamond coatings.

To improve the mechanical properties of the gold coating we explored the possibility of introducing diamond particles into the film. These studies were carried out on a flat plate made of polystyrene (*Figure 2d*). synthetic diamond powder ACM brand 5 (Russia), obtained by detonation method, was used. The powder comprised prismatic diamond particles with an average size of 0.5-1.0 microns [28].

After creating a sorption layer of gold chloride solution on the surface of wet plate by compressed air, synthetic diamond particles were sprayed on this surface. Diamond particles were fixed by the gold film in the surface layer formed of the material (*Figure 6, Table 6*). The carbon content on the surface was 83.47%. After deducting the amount of carbon attributable to the polymer plate (79.22%), we got a diamond content of 4.25% in the film. Having increased the diamond particles on an additional layer of gold, we can obtain a composite gold-diamond coating.

The hardness testing of samples showed that the diamond-containing composite coating increased the hardness of the sample of 52 units HB (data not shown). Also copper positively influenced the hardness of the coating, but this effect was not significant.

4. Conclusion.

The gold deposition technology on the dielectric film was based on ion gold-phosphine gas. In this process, initially, a sorption layer of gold chloride solution was created by priory wetting the surface of the product. Depending on the concentration of gold in the solution a film thickness between 0.03 microns and 0.5microns was formed. The study of the film surface using a scanning electron microscope revealed that the reaction product in this case was pure gold.

When copper chloride (II) was administered into gold chloride solution, reduction of both components occurred. The reduction of copper ions with phosphine led to formation of copper phosphide, which is consistent with the mechanism proposed in [26]. Thus, using this technology, we can get a combination of gold-copper phosphide coating.

Combined gold containing coating can also be obtained by spraying solid particles. These particles were deposited on the surface of the product containing sorptive solution of gold chloride, and fixed with gold, formed in the reduction of the phosphine gas. In this paper, this method was tested for gold-diamond coatings. As a results of this process we obtained a coating containing 4.25% of diamond.

5. References

- [1] goldomania.ru/menu_
- [2] [golden-inform.ru/prochee/...](http://golden-inform.ru/prochee/)
- [3] <http://www.gold.1prime.ru/bulletin/show.asp>.
- [4] M.A. Dacoyan, I.Ya. Pal'mskaya, E.Ya. Sacharova, Electrochemical coating technology, 1989, Pages 231-237.
- [5] J.V. Kudryavzev. Composition of electrolytes for gold coatings and their preparation methods. Patent. RF. № 2501891 MPK: C25D. Published 20.12.2013.
- [6] Specification for Electroless Nickel / Immersion Gold (ENIG) Plating for Printed Circuit Boards. IPC-4552. July 2002.
- [7] S. Shkundina. New processes and materials in the manufacture of printed circuit boards // Technology in the electronics industry. № 4, 2009.
- [8] B. Lung, G.K. Burkat, V.J. Dolmatov, V.J. Saburbaev. Preparation of composite gold containing coatings. Patent. RF № 2191227 MPK: C25D3/48, C25D15/00. Published 20.10.2002.
- [9] N. Samsonov, N. Dudkin, Gold trajectory-2. Expert of Siberia. № 22, 2014.
- [10] Patent R U 2 3 7 8 0 4 8 C 2
- [11] E.A. Kononova. Preparation, criostability, adsorptive and bactericidal properties of nanoparticles Ag, Au, Ag-Au sols and carriers. Thesis. Moscow. 2000.
- [12] Patent, Japan № 5 - 53879, Published 08.11.93.
- [13] Patent, USA № 5318687, Published 06.07.94.
- [14] Patent, Germany № 4204087, C 25 D 3/48, Published 19.08.93.
- [15] Patent, Switzerland № 680370, C 25 D 3/56, Published 14.08.92.
- [16] Patent BU №10471, MPK C25D 3/02, Published 30.04.2008.
- [17] A.I. Stognii, N.N. Novizkii, S.D. Tushina, S.V. Kalinnikov. Preparation method of ion beam sputtering with oxygen and optical properties of ultra-thin gold films. J. Technical Physics. V.73 (6), 2003, pages 86-89.
- [18] P.S. Mel'nikov. Reference plated in mechanical engineering, 1979.
- [19] Patent US 4999054, 1991.
- [20] A. Medvedev, J. Nabatov, P. Semenov, S. Shkundina. Immersion plating solder. J. technology in the electronics industry, №2, 2010.

- [21] T.N. Borob'eva, T.N. Vrubleva, T.N. Vrublevskaia, A.V. Vengura. The solution for the electroless deposition of gold films on a nickel coating. Patent BUN \# 10283, MPK C23C18/31, Published 18.02.2008.
- [22] A.A. Bessonov, N.B. Morozova, N.V. Gelfond, P.P. Semyannikov, S.V. Trubin, Yu.V. Shevtsov, Yu.V. Shubin, L.K. Igumenov. Dimethyl-gold(DI) Carboxylates as New Precursors for Gold CVD // Surf. Coat. Tech. Vol. 201, 2007, Pages 9099-9103.
- [23] A.S. Kuch'yanov, A.I. Plehanov, I.K. Igumenov, B.M. Kuchumov, R.G. Parhomenko, S.V. Trubin. A method of deposition of gold nanoparticles on the silica microspheres, based on the thermal decomposition of volatile compounds of gold. Patent RF \# 2489230 MPK: B22F9/12. Published 10.08.2013.
- [24] A.J. Tuleushev, V.N. Lisizin, J.J. Tuleushev, V.N. Volodin, S.N. Kim. Patent RF \# 2214476 MPK: C23C14/16. A method of forming a coating of precious metals and their alloys. Patent RF \# 2214476 MPK: C23C14/16. Published 20.10.2003.
- [25] M.S. Sataev, Sh. T. Koshkarbaev, A.B. Tasboltaeva. Metallization of textile industry Math. universities. The technology of the textile industry. \# 6 (348), 2013, .Pages C102-104.
- [26] SH. T. Koshkarbaeva, S.Z. Nauryzova, M.S. Sataev and A.B. Tleuova. Low-temperature Gas-phase Metallization of Dielectrics. Oriental journal of chemistry 2012; 28(3):1281-1283.
- [27] M.S. Sataev, S.T. Koshkarbaeva, A.B. Tleuova, S. Perni, S.B. Aidarova, P. Prokopovich. Novel process for coating textile materials with silver to prepare antimicrobial fabrics. Colloids and Surfaces A: Physicochemical and Engineering Aspects Volume 442, 1 February 2014, Pages 146–151
- [28] MS Sataev, ST Koshkarbaeva, S Perni, SZ Nauryzova, P Prokopovich. A galvanic-chemical method for preparing diamond containing coatings. Colloids and Surfaces A: Physicochemical and Engineering Aspects.480 (2015) p. 384-389
- [29] MS Sataev, P.Prokopovich, Sh.T. Koshkarbaeva, S. Perni, P.A. Abdurasova, A.A. Saipov. Method of application of gold metal on the surface of various materials. Patent KZ 2016 /0491.1, 08.06.2016.
- [30] Sh.T. Koshkarbaeva, Development of technological processes based on the synthesis of copper phosphide films. Thesis. Shymkent, 2002.

Tables

Table 1. Elemental analysis of the gold film of the cotton fabric sample.

Element	Content, %(weight)
C	6.52
N	2.88
O	2.18
Au	88.42

Table 2. Elemental analysis of the gold film of the porous PVC sample.

Element	Content, %(weight)
C	20.72
O	5.92
Cl	14.68
Au	58.67

Table 3. Elemental analysis of gold film obtained by combined precipitation of copper.

Element	Content, %(weight)
C	31.67
O	27.26
Si	0.55
Cl	0.41
Ca	0.71
P	1.37
Cu	5.20
Au	32.83

Table 4. Elemental analysis of gold film containing diamond particles.

Element	Content, %(weight)
C	83.47
O	1.45
Cl	0.15
Au	14.93

Figure captions

Figure 1. *Separate stages of the gold coating process and changes observed of the surface layer.*

a-initial sample; b-sample after coating with gold chloride by adsorption; c- sample after drying of the adsorptive layer; d-sample after reduction reaction of gold chloride by phosphine gas; e-sample after washing from by-products.

Figure 2. *Gold coatings of samples of different materials:*

a – cotton fabric gold coated; b – PVC gold coated; c – cotton fabric gold-copper coated; d– PVC gold-diamond coated.

Figure 3. *SEM image and EDX data of the gold film of the cotton fabric sample.*

Figure 4. *SEM image and EDX data of the gold film of the porous PVC sample.*

Figure 5. *SEM image and EDX data of gold film obtained by combined precipitation of copper.*

Figure 6. *SEM image and EDX data of gold film containing diamond particles.*

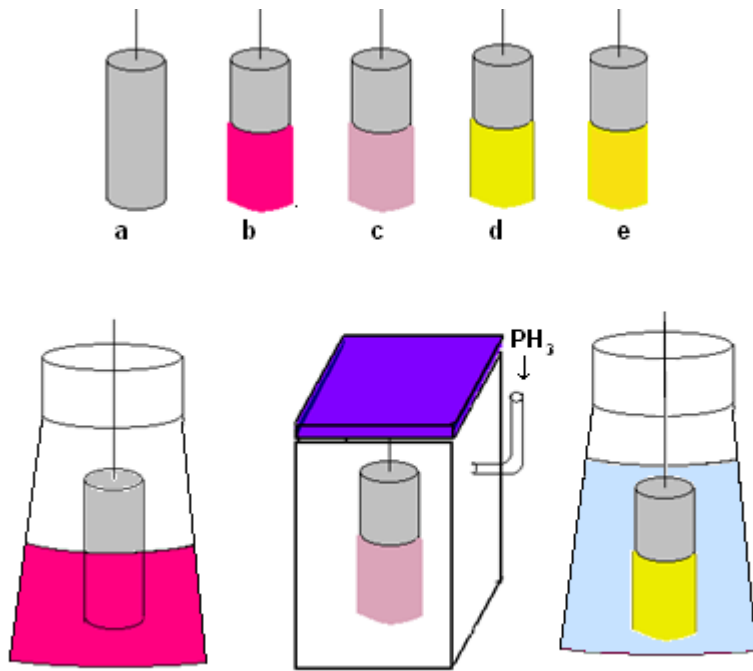


Figure 1.

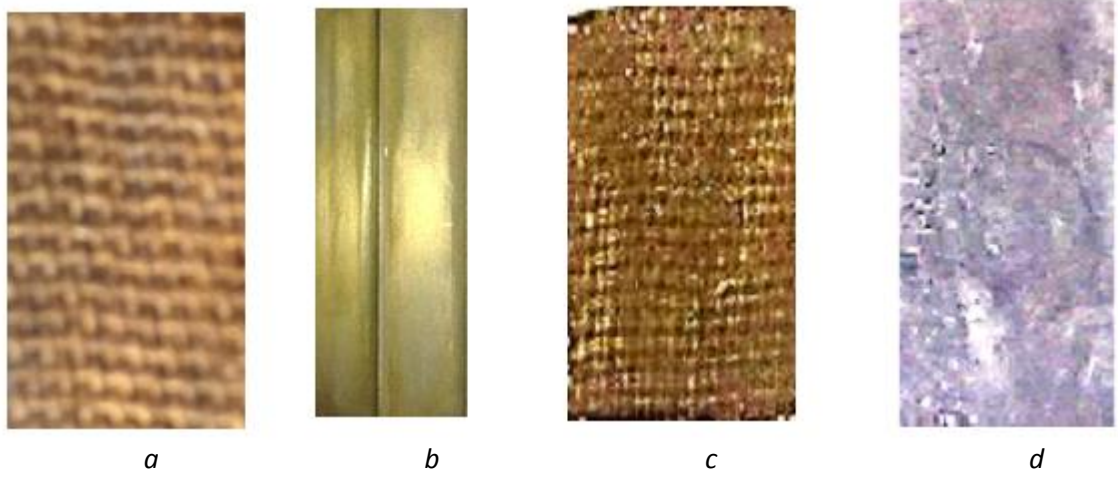


Figure 2

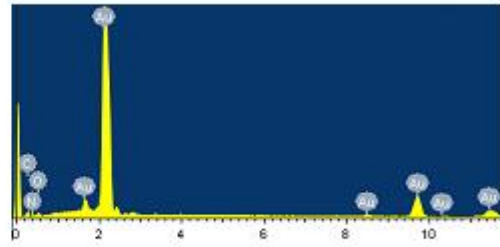
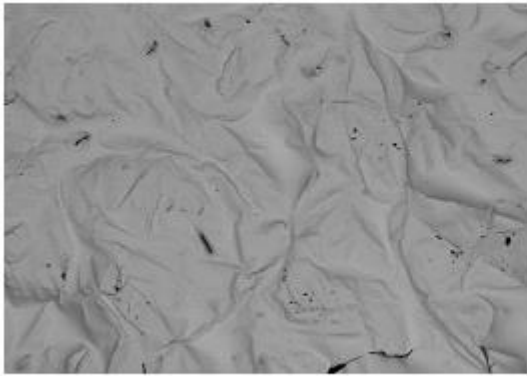


Figure 3

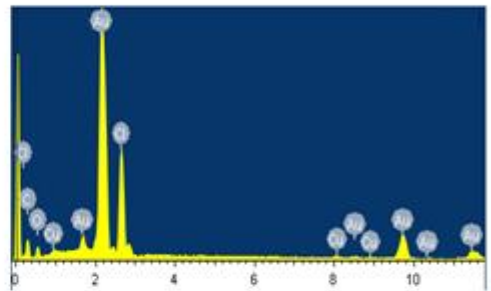
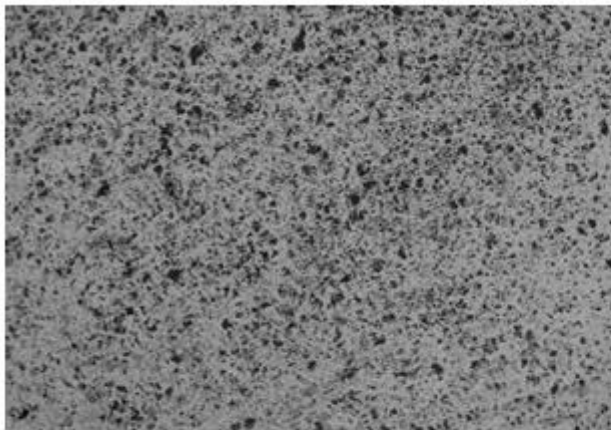


Figure 4

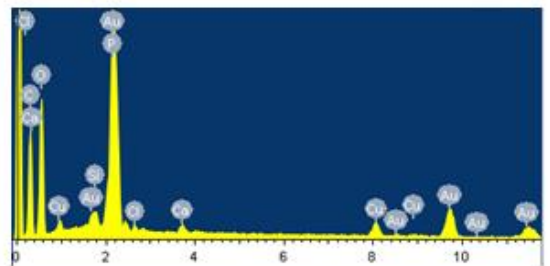
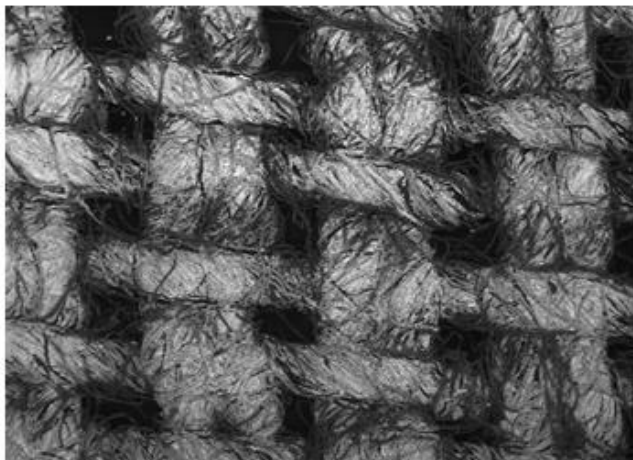


Figure 5

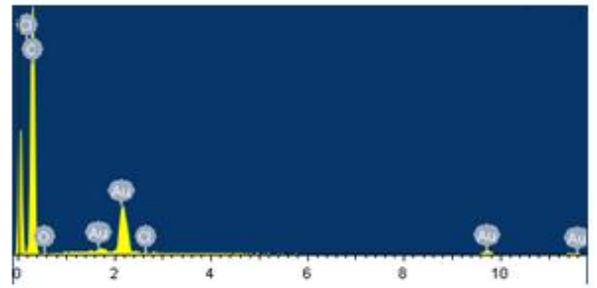
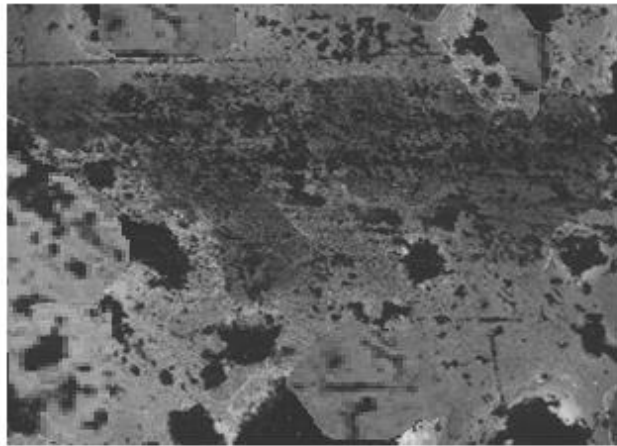


Figure 6