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Copper metallization for functional application

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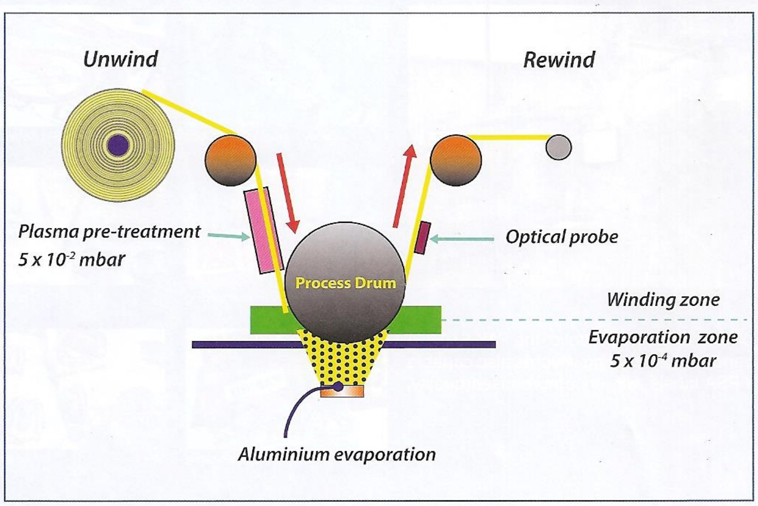
Vacuum web metallizing of aluminium is widely used in the packaging and other industries for oxygen and water barrier applications. However, there is a continuous demand now for other niche metallized products that can be by standard metallizers for other applications. Copper metallizing is considered to be an emerging product for different advanced market applications.

The demand for higher speed vacuum metallizing coupled with higher copper deposits has focused attention on improving the uniformity and durability of the deposited layer across the width and down the length of a moving film web. This requires the design of special evaporation sources and monitoring techniques with associated closed loop feedback systems. The use of plasma pre-treatment is very important to improve substrate surface energy and hence, reduce problems of banding and non-uniformity. This present article evaluates the process of vacuum metallizing of copper on flexible films and presents some functional applications.

Figure 1: Schematic of vacuum web metallizing



Source: Idvac Ltd.

Introduction

The technology and applications of vacuum web metallization has entered many markets including packaging and holographic. As an example, the utilisation of aluminium vacuum metallization to replace the former trend of using aluminium foil for packaging.

Most vacuum web metallizers used worldwide are mainly designed for aluminium metallization. However, the trend in the market is also moving towards the use of other coatings for added value products. One of the new obvious candidates for added value coating is copper metallization that can be produced in a standard vacuum metallizer. Recent interest in copper metallization is mainly due to its optical, structural, functional and anti-bacterial characteristics. This opens the door for new market applications.

Copper has some special characteristics including bright lustre. The ratio of copper electrical conductivity to that of aluminium is approximately 5:3, and the thermal conductivity ratio is approximately 2:1, resulting in improved electrical performance, reduced Joule heating, and better heat transport. Copper is also a good heat reflector and has a low electrical sheet resistance. A thin coating of copper has very wide applications in flexible printed circuit boards, solar window films, electromagnetic shielding, thin conductive electrodes for electrical circuits, holographic, anti-bacterial and other niche applications.

"Most vacuum web metallizers used worldwide are mainly designed for aluminium metallization."

This paper reviews the vacuum metallization process used in standard vacuum web metallizer to deposit copper. Moreover, this article describes some parameters that can influence the structure, uniformity and final property of the deposited copper onto a moving flexible film. Most of the metallizing technologies discussed are relevant to product applications such as those mentioned above.

Copper metallization process

Copper is used extensively in the microelectronics industry. For example, printed wiring board applications utilize large quantities of copper as electrodeposited foil. Thick copper inks are incorporated into ceramic green sheets to form low temperature cofired ceramic interconnect structures. These examples demonstrate the value of copper foils and thick coatings at various levels of the electronic packaging hierarchy.

At present there are many techniques utilized to metallize thin and thick copper coating including:

Vacuum metallizing process

Metallization is a process where a metallic layer is deposited on a nonmetallic (plastics, glass, ceramics, paper, cardboard) or metallic substrate. The aim is to improve the usefulness of a product by the coating (surface refinement). The metallization by vacuum technology uses the condensation of a metal vapour on the object to be coated. This vapour is generated within a vacuum, and diffuses within this vacuum. In vacuum web metallizing, roll to roll of flexible film is metallized inside the vacuum chamber at high speed, shown in figure 1.

Modern vacuum web equipment for the metallization of various polymeric films requires the use of high-performance evaporation sources to evaporate metals such as aluminium or copper at fast line speed. For the evaporation of aluminium, ceramic boats are used to permit high speed of evaporation/ deposition onto a moving film.

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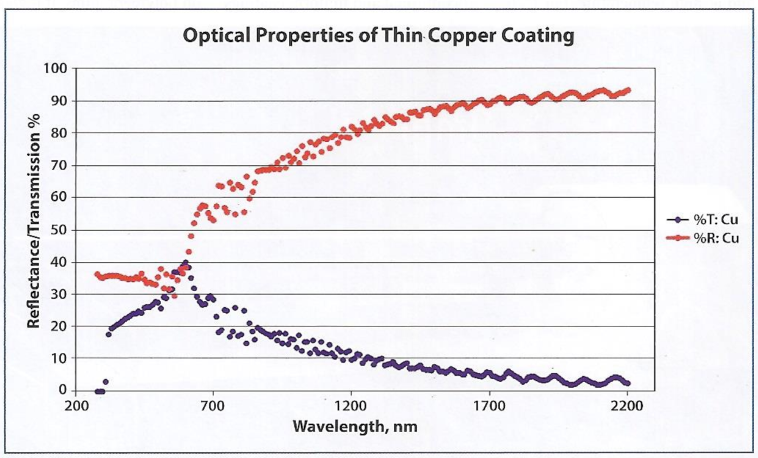
The new generation of aluminium metallization equipment for packaging applications requires a line speed of more than 10 m/sec (32.8 ft/sec) with coating thickness uniformity below ±5%. For solar window film application the uniformity requirement is below ±2%. Uniformity is one of the most important characteristics reflecting machine performance. Poor uniformity often leads to banding effect on metallized film. This is an important issue in copper metallization since this will show as bands with different copper shades. Uniformity is influenced by many parameters including film surface wettability (i.e surface energy), level of vacuum in the evaporation zone, the design of the evaporation source and control of the evaporation rate. The employment of a plasma pre-treatment source inside the metallizer is important to improve substrate surface wettability and uniformity. For the metallization of copper special evaporation sources have to be used to meet a similar spec to those for aluminium metallization. High line speed, good uniformity and adhesion have to be achieved for high quality copper metallization. There have been some attempts to use graphite, standard ceramic boats, molybdenum or tantalum to evaporate copper but with minimum success (figure 2). This is due mainly to the wettability problem on the surface of such boats and the requirement of high power to evaporate the material.

Idvac Ltd. has developed its own process to deposit copper inside a standard vacuum web metallizer using specially treated resistive evaporators. This does not involve painting of the evaporator surface with special coating to promote wettability and also does not require the need for expensive power supplies or transformers, as shown in figure 3.

Copper wire is fed continuously onto the special evaporators for a continuous metallization processes at an average speed of 200 m/min (656 fpm) to produce 1.6 OD copper thickness. The special evaporators life is similar to that for aluminium metallization boats. The productivity of such evaporators is high and the uniformity can be within +-5% along width and length of web.

Source: Idvac Ltd.

Figure 3: Thermally metallized copper



Source: Idvac Ltd.

Figure 4: The optical characteristics of thin copper coating

■ Electroplating and Electroless plating; copper is electroplated using wet chemicals inside trenches and holes in insulators. A thin continuous copper seed layer is needed before electroplating copper. A variety of plastics, such as polythene, Teflon, polysulfone, polypropylene, acrylonitrile-butadiene-styrene (ABS), etc. can be wet metallized with copper. In the electroless procedure, deposition happens spontaneously on any surface without requiring any external electrical potential and processing. However, it is more difficult to control the process with regards to film thickness and uniformity. In addition, it is a multi-step procedure requiring a long deposition time and complex chemical solutions. Some of these chemicals are costly and environmentally hazardous.

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■ Physical vapour deposition (vacuum metallizing processes); this includes vacuum thermal evaporation and sputtering. This technology is dry and environmentally friendly. The evaporation of copper is carried out inside a clean vacuum environment.

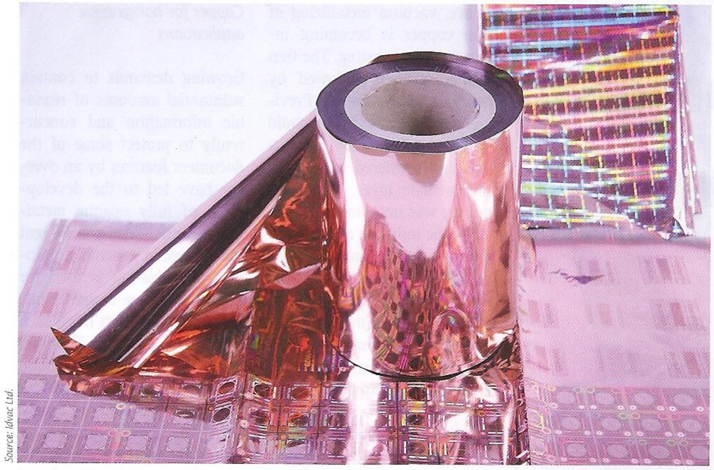
■ Chemical vapour deposition (CVD); using precursors containing copper in a plasma environment and at high temperature. For CVD, the morphology of copper films can sometimes be improved by adding a second component to the growth gas. However, this may tend to increase the resistivity of the coating, because copper oxides are also deposited. Therefore, this approach is not suitable for applications that require very thin (<10 nm) copper coatings with high electrical conductivities.

■ Atomic layer deposition (ALD); this new technique is known for depositing conformal and continuous films onto structures with very high aspect ratios. It is one of the most promising techniques to enable nanoscale device fabrication due to its precise thickness control of conformal and uniform coatings over large areas. ALD processes have been developed for many metal oxides, nitrides, and sulphides, while the use of ALD for metals have been hindered mainly by the chemicals used.

For some microelectronic applications such as flexible printed circuit boards combination of some of the above processes are used to achieve the final product. For example, sputtering is used to deposit seed layers to provide the adhesion for the thermally metallized copper on the substrate.

In this article vacuum metallization of copper will be discussed because it can offer a dry process for the production of copper coating on polymeric films at high speed.

Figure 2: Wettability problem of copper on graphite boat



| *Figure 5: Metallized copper for holographic applications*

Applications of copper metallized films

At present there are many functional applications for copper metallized films. Some applications will be described briefly:

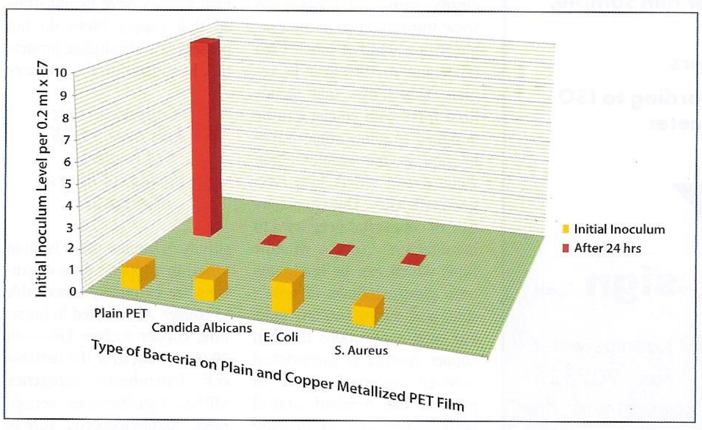
Copper metallization for flexible printed circuit boards

At present, vacuum metallized copper is used on films such as Polyimide, PI (e.g. Kapton) for the manufacturing of flexible printed circuit boards (FPCB). Polyimide / PI is an advantageous substrate material for flexible printed boards, ribbon cables and multilayer PCBs because it combines mechanical strength, temperature and chemical stability with good dielectric properties.

High specifications are placed on the reliability of PCBs used in these applications, many of them being safety related. In particular, the copper conductors must adhere firmly to the polyimide to withstand the thermo-shock from the soldering during the PCB assembly and the stresses from the vibrations, shocks, temperature, and humidity fluctuations during the device exploitation.

> *"Currently, copper-polyimide laminates are made almost exclusively by adhesive bonding."*

Currently, copper-polyimide laminates are made almost exclusively by adhesive bonding. However, adhesives can affect the electrical and mechanical properties of the system.



| *Figure 6: Effect of metallized copper on bacterial growth*

Hence, vacuum metallizing of thin copper is becoming increasingly interesting. The thin copper layer is followed by galvanic reinforcement. Previously, sufficient adhesion could only be achieved by using a vacuum sputtered chromium intermediate layer. This technology was not widely accepted by the industry, as the chromium layer requires an additional etching process during the PCB production.

The surface of the polyimide can also be chemically modified by using plasma to form a chemical compound with metallized copper, thereby resulting in a dramatic adhesion improvement. Compared with wet chemistry, the plasma-chemical modification of the surface has the advantage that it can be combined with vacuum metallized copper deposition in a single unit and from roll to roll.

> *"Holographic embossed films metallized by copper exhibit an aesthetically appealing copper lustre."*

Copper for solar window films

The transmittance and reflectance spectrum of copper metallized polyester film is shown in figure 6. It can be clearly seen that copper has some transmittance in the visible region while it has a high reflectance in the near IR region. This shows that metallized films with copper can be designed to allow some transmission in the visible region while it can reflect heat with good efficiency. This characteristic of copper has been used to manufacture solar window films which can be laminated onto glass windows to reflect solar heat during summer time. For such applications the thin copper coating is sandwiched between dielectric layers to provide the required optical performance and to increase environmental durability.

Copper for holographic applications

Growing demands to contain substantial amounts of readable information and concurrently to protect some of the document features by an overlay have led to the development of fully opaque metallized and semi-transparent holograms. In general, aluminium metallization is used for highly reflective images while high index coatings (HRI) such as Zinc Sulphide or Titanium Oxide are used for see-through security documents such as passports and identity cards. However, there is a growing requirement to replace aluminium with other functional and decorative coatings such as copper to provide high visual lustre to fight counterfeiting. Holographic embossed films metallized by copper exhibit an aesthetically appealing copper lustre. At present, copper is used for security documents and to make the metallic thread in some banknotes.

Copper for microbial protection

Copper is considered to be safe for humans, as demonstrated by the widespread and prolonged use by women of copper intrauterine devices (small contraceptive device). Also animal studies have demonstrated that copper fibres do not possess skin sensitizing properties. In contrast to the low sensitivity of human tissue (skin or other) to copper, micro-organisms are extremely susceptible to copper. As reported in literature, copper surface kills over 99.9% of bacteria (Escherichia coli, Enterobacter aerogenes, MRSA, Pseudomonas aeruginosa, Staphylococcus aureus) during 24 hours of exposure.

> *"Copper surface kills over 99.9% of bacteria during 24 hours of exposure."*

Source: Idvac Ltd.

| *Figure 7: Effect of copper metallized and non-metallized PET film on bacterial growth*

In order to test such findings, Idvac Ltd., has conducted its own investigation of the anti-bacterial properties of metallized copper on polyester film. Vacuum metallized copper on polyester film has been tested on three types of organisms: Candida albicans, E-Coli and S.aureus. E-Coli is responsible for food poisoning, while S.aureus cause skin infection in wounds with a long lasting effect. Heavy growth rate of organisms was observed when these organisms were grown on uncoated plain PET film. However, the growth was inhibited on the vacuum metallized copper on PET film in a short time. However, the different results are shown in figure 6 and figure 7. These findings would also suggest a possibility of metallizing textile materials with copper for special anti-bacterial applications.

Conclusion

Vacuum metallizing of copper on flexible films has received so much attention because of its functional applications. Vacuum metallizing is a dry and environmentally friendly process that does not use any wet chemicals. Standard vacuum web metallizers can be used to produce such coatings with minimum modification. However, process control will require the selection of films with minimum moisture level and metallizers with good vacuum levels and cooling capabilities. In order to prevent banding and improve uniformity plasma pre-treatment is highly recommended.

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