

# Highly Reflective Coatings

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## 1. ABSTRACT

This paper provides a comprehensive review on highly reflective coatings. A highly reflective coating is a thin film or layers of films that are deposited on a substrate to enhance the reflecting property of the substrate. These highly reflective coatings show great scope for use in products that are sensitive to damage caused by heat. In this paper we cover different types of highly reflective coatings - metal and dielectric. Nanoparticles based on metals are also being used to coat substrates to allow maximum reflectance. Dielectric coatings reflect light by constructive interference through the different layers of the dielectric material. Three different types of methods for synthesis of highly reflective coatings have also been discussed. The paper also gives a brief on different areas of applications of these highly reflective coatings.

**Keywords:** Highly reflective coatings (HR), Dielectrics, Radiation, Metal nanoparticles, hybrid coatings

## 2. INTRODUCTION

Silver is the most talked about when it comes to high reflectivity value. Silver mirrors have been manufactured since a long time and used in the household but here we do not only talk about the reflection of visible wavelengths of the electromagnetic spectrum but also UV and IR wavelengths. Reflecting the wavelengths underlying UV and IR region is of great importance when we talk about the use of products that can get damaged by heat. E.g. Food products, glass windows, paints etc. High reflectors also have applications in photovoltaic cells and lasers to optimize power consumption. Optical mirrors are mirrors coated with highly reflective materials that reflect the light of desired wavelength and are only coated on the top surface unlike household mirrors that are coated on both the sides. Technology with highly reflective coatings becomes essential to maximize the shelf life of such products. Solar radiation mainly consists of UV (5%), IR (49%) and VIS (46%) wavelengths. Different metallic and non-metallic nanoparticles are used for this

purpose. Metallic silver (Ag), gold (Au) and aluminum (Al) are the most widely studied as highly reflective materials. Other materials such as different nanocrystalline metal oxides -TiO<sub>2</sub>, ZnO, MgO and Al<sub>2</sub>O<sub>3</sub> are widely used as IR reflectors. MgF<sub>2</sub> and AlF<sub>3</sub> protected Al films have reflectors in the UV spectral region. In this paper a detailed discussion of highly reflecting coating materials, working mechanism, classification, properties, methods of manufacture and applications is done.

## 3. TYPES OF HIGHLY REFLECTIVE COATINGS

### a) Metallic Coatings

Metals are widely used to coat various substrates to allow maximum reflectance. Aluminium and silver are excellent reflectors in the visible region, their reflectance being 0.90 and 0.95 respectively. The reflectance of a metal coat can be easily determined with the help of refractive indices using the following formula:

$$R (\%) = \frac{(n - 1)^2 + k^2}{(n + 1)^2 + k^2} \times 100$$

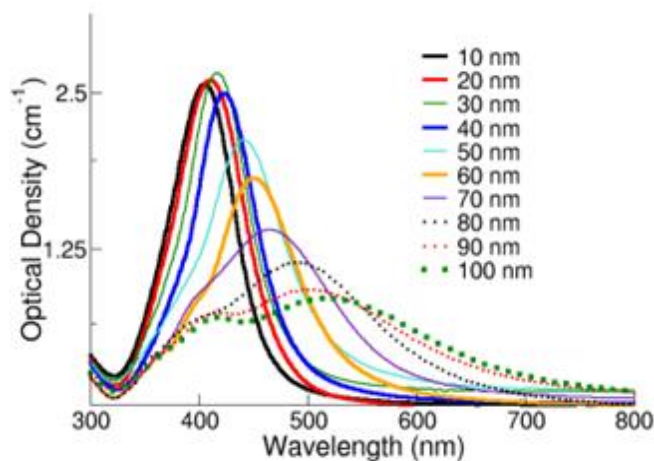
Where, n= Refractive index, k= Extinction coefficient and R is reflectance in %.

A list of values of n and k are obtained for ultraviolet (0.2 and 0.3 μm), visible (0.4 to 0.7 μm) and infrared wavelengths (1 to 10 μm). When a metal has k value greater than n, it appears shiny. e. g. silver. Since the wavelengths increase as we move from visible to IR, the values of k and n increase and the reflectance increases.

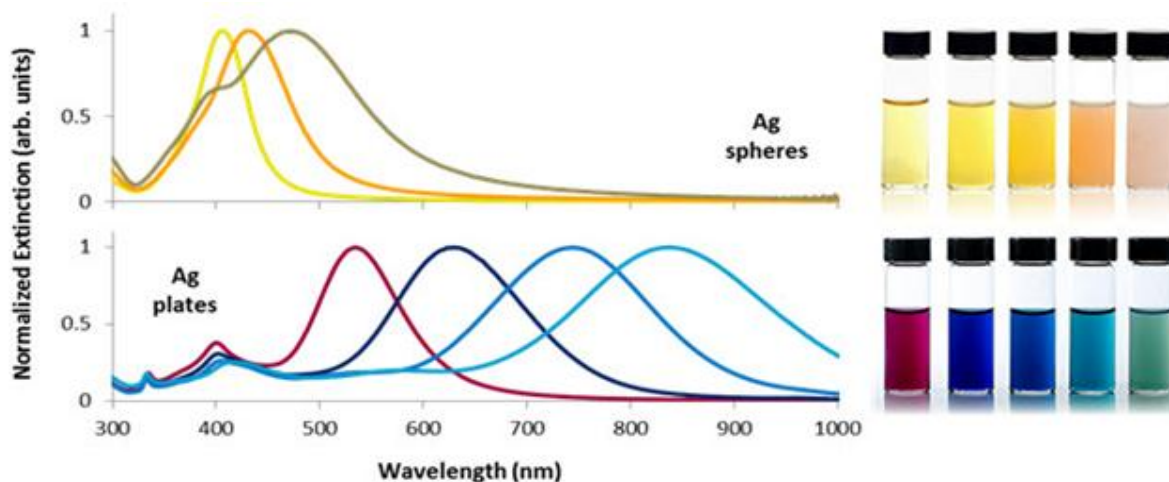
Metal nanoparticles absorb and scatter light with unique efficiency. Metals have a sea of conduction electrons present at the surface. When electromagnetic waves strike metal surface of any type, the surface electrons start oscillating in a collective manner. Such oscillating motion of surface electrons is known as a surface plasmon resonance (SPR). 'Plasmons' are collective oscillations of free electrons in

metals which occur at a well-defined frequency. A plasmon is also described as an electron cloud displaced from its equilibrium state in the lattice. The reflectance can be altered by means of adjusting particle size, shape and the local refractive index. The plasmons present in the bulk do not get

excited, only the presence of an open surface promotes the existence of various plasmon oscillation modes which are excited by any electromagnetic radiation.



**Figure 3.1** Absorption spectra of Ag nanoparticles with varying diameter over visible region[8]



**Figure 3.2** Absorption spectra of Ag nanospheres and Nanoplates over visible region[10]

**Effect of various parameters on optical properties:**

1. Optical properties of any metallic nanomaterial largely depend on the diameter of its nanospheres. Fig 3.1 shows the variation of absorbance/ Optical density with changing particle diameter.
2. Spherical And plate like nanocrystals of silver give different absorption spectra in the visible region as shown in fig 3.2.
3. A shift towards red (Larger wavelength) when the surrounding medium is denser and to blue (Shorter wavelength) when the surrounding medium is rarer is observed.

4. A change in optical properties is observed when the nanoparticles aggregate and the conduction electrons become delocalized and shared with other atoms in the close proximity. Due to this, the SPR shifts to lower energies.

**b) Dielectric coatings**

Dielectric coatings reflect light by constructive interference through the different layers of dielectric material. Anti-reflective coatings are also based on the same principle but destructive interference is observed. A reflectance greater than 99.99999% can be obtained over a selected spectral range by

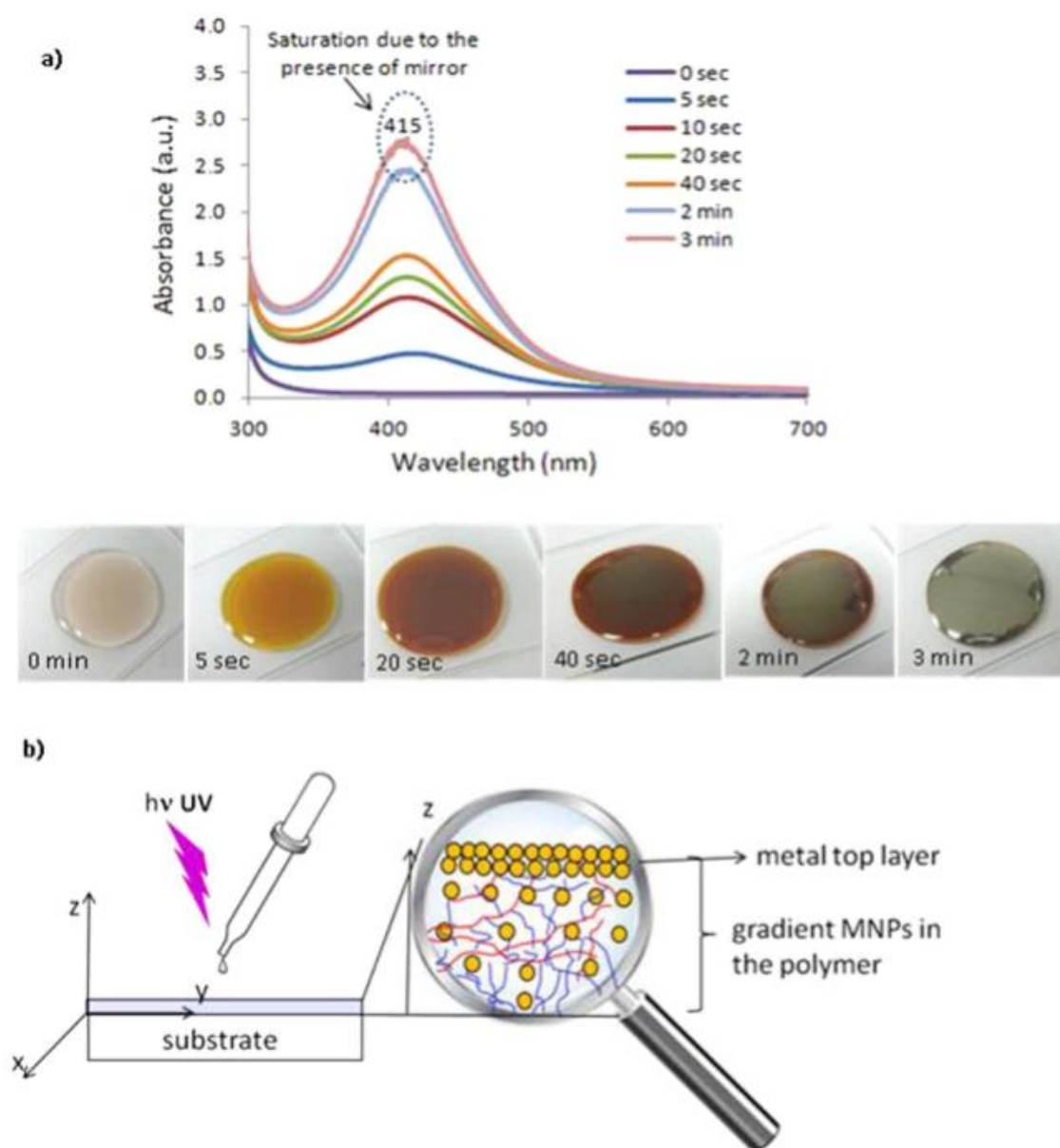


## 2) Highly reflecting metal coatings of silver nanoparticles by assembling in polymer matrix

Light induced synthesis of Ag-polymer nano scale assemblies is done to obtain a HR metal coating.  $\text{Ag}^+$  ions act as a photosensitive precursor, UV source is the photo-source and acrylate monomer acts as a polymer matrix precursor. 0.5% by weight of  $\text{Ag}^+$ , 5% by weight of photosensitizer and acrylate monomer act as a photosensitive mixture which is let to stand for 1hr at room temperature with continuous stirring by automatic means. Free radicals stem out from the proper breakdown of light sensitive precursor which produce silver nanoparticles out of  $\text{Ag}^+$  ions by reduction. Along with this, the radicals start the light-initiated polymerization of monomers of acrylate, resulting in the forming of a polymer

matrix. Proper kinetic rates and its control can give desirable Ag-polymer nano formations. [12]

As the time of irradiating with UV light increases, formation of more and more silver nanoparticles takes place which provides a filter to the light entering due to absorption of it. Hence, with the progressing of time, the reduction reaction is kept at the top surfaces and the surface at the top turns reflective as aggregation of more and more silver nanoparticles takes place. After 2-3 minutes of exposure, the coating turns into a smooth reflecting Ag surface. TEM micrograph shows that the size of nanoparticles inside the outer silver mirror layer (250 nm thick) is 10-11 nm [12] and they are spheres which are homogeneous in size and are evenly dispersed.



**Fig.:** a) Absorption spectrum of Ag nano formations in the polymer matrix along with images of the coating with progression of time. b) Schematic diagram of formation of silver nano formations.

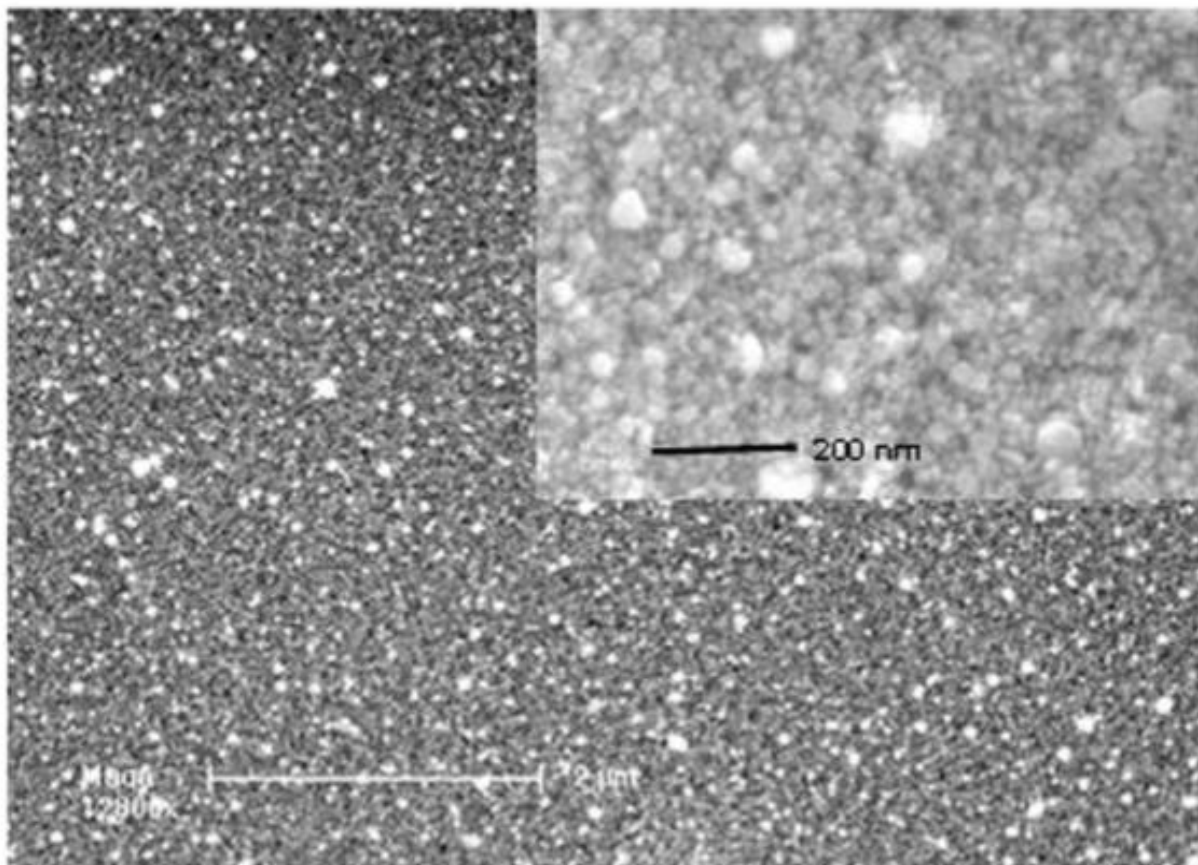


Fig: SEM image of the surface of the silver mirror [12]

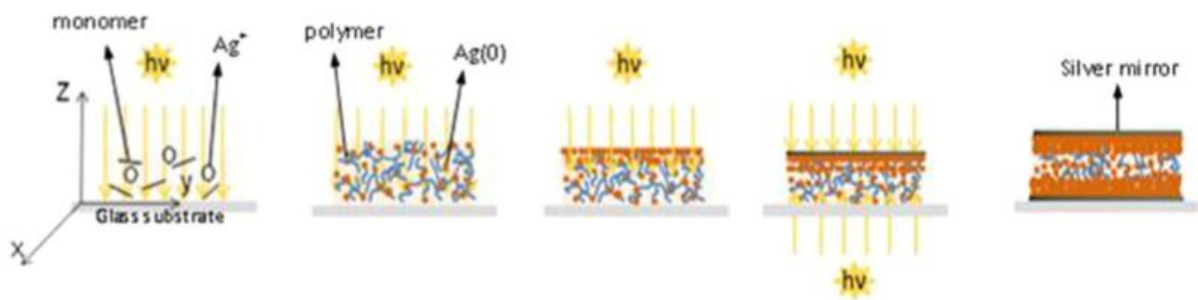


Figure 7. Schematic representation of the photo-induced synthesis and organization of silver@polymer nanoassembly.

### 3) Hybrid HR coatings (Inorganic + Organic compounds)

Hybrid HR materials have two components, organic material in which inorganic nano sized particles get evenly dispersed. The inorganic nano sized particles are mostly those of metals (eg- gold, palladium, silver etc.) and the organic phase is a matrix of polymers. Metals form clusters in the organic phase because of which suspension stabilizing polymers are used such as poly(vinyl alcohol), polyvinyl pyrrolidone, poly(amide imide) etc.

Deposition of certain metals like silver can be done in one stage internal, self-metallization process. Silver is chosen

because of its excellent reflecting property in the visible and IR spectrum and the polymer along with this is poly(amic acid)-polyimide which exhibit appreciable thermal and chemical stability (which is necessary in thermal metallization process because Ag catalyzes the oxidation of organic compounds).

#### Synthesis:

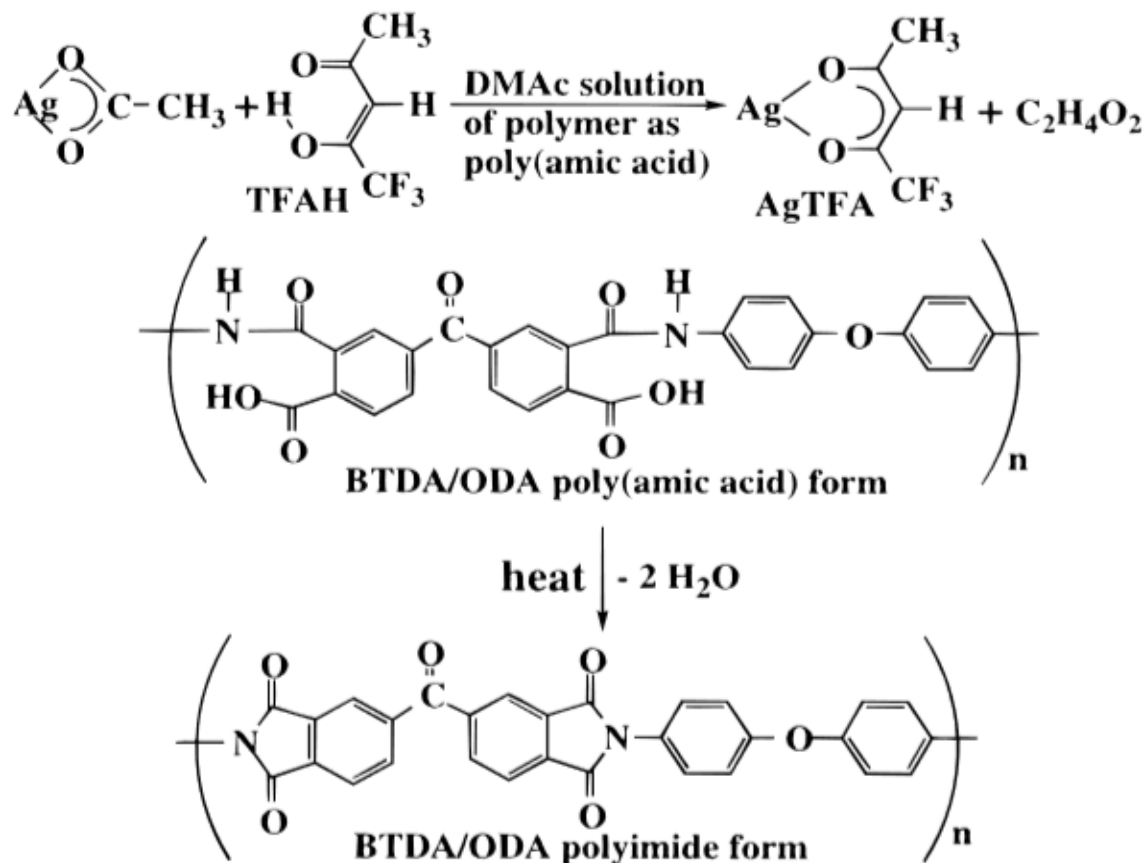
Silver(I) Acetate reacts with 1,1,1-trifluoro-2,4-pentanedione (TFAH) in Dimethylacetamide(DMAc) to give (1,1,1-



trifluoro-2,4-pentanedionato) silver(I) complex,  $AgTFA$  in the form of solution already present. [13]

A solution of poly (amic acid) form of BTDA/ODA in Dimethylacetamide (DMAc) is added to the formed  $AgTFA$  solution. A thick consistency solution of silver(I)-poly(amic

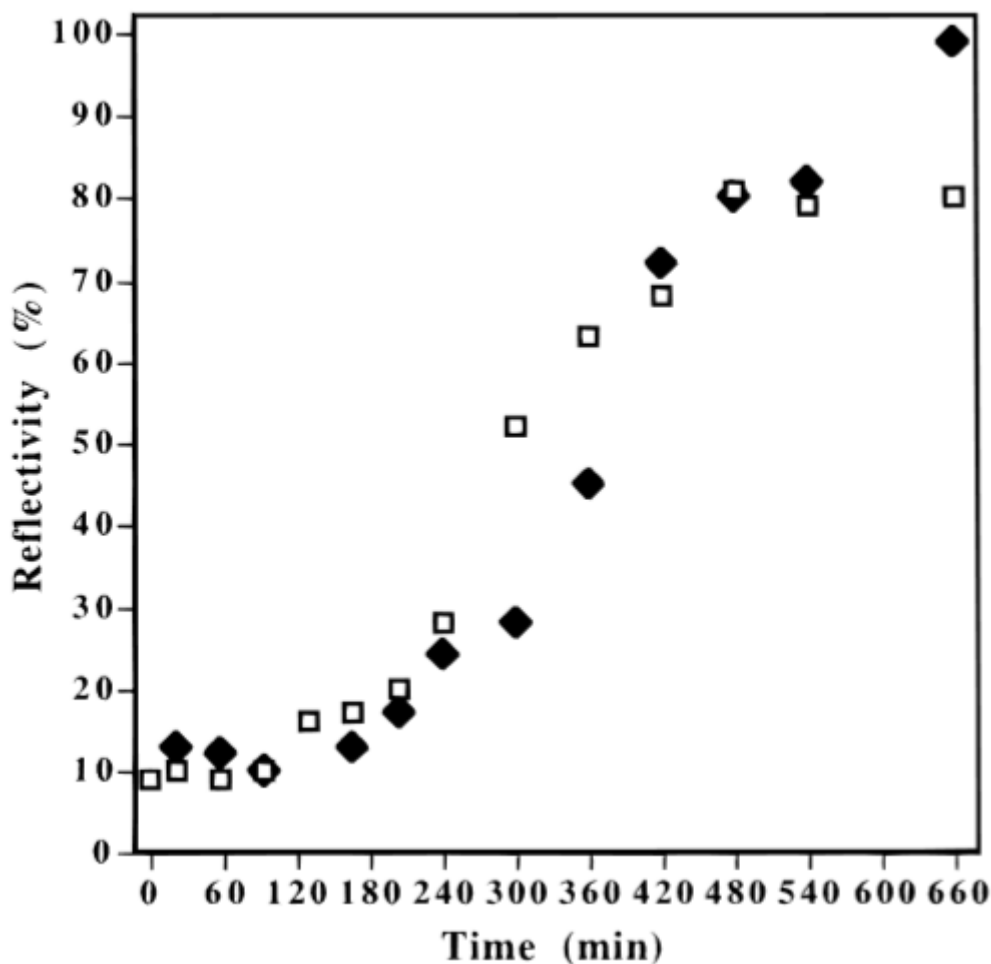
acid) is obtained after which a film is casted. Heated curing of this film for 7 hrs at  $300^{\circ}C$  reduces the  $Ag^{+}$  which is joint with the cycloimide of the amic acid. The polymer after this imidizes to give  $Ag(0)$  atoms form aggregates on the surface to give a highly reflecting and conducting film. [13]



**Table 1.** Reflectivity, Thermal, and Resistivity Data for (1,1,1-Trifluoro-2,4-pentanedionato)silver(I)-BTDA/ODA Films cured to  $300^{\circ}C$  for 7h and Cast on a Glass Plate (Films 1-3) and on a Parent Polyimide Base (Film 4)

film no.	% silver (calcd) <sup>a</sup>	reflectivity of silvered films <sup>b</sup> (as a function of angle)					$T_g$ °C (DSC)	CTE (ppm/K)	surface resistivity <sup>c</sup> (polished film) ( $\Omega/sq$ )	tensile strength (Ksi)	modulus (Ksi)
		20°	30°	45°	55°	70°					
1	0	not applicable					275	42.8	$7 \times 10^{15}$ (air) $2 \times 10^{17}$ (glass)	19.7	450
2	13.0	98	97	97	95	91	276	34.3	<0.1	19.7	474
3	12.8	98	98	98	99	92	270	33.0	<0.1	20.2	468
4	12.8	95	95	94	92	91	273	32.8	<0.1	19.3	445

Table: Reflectivity, Thermal and Resistivity data of the film obtained after curing. [13]



Graph: Reflectivity as a function of curing time [13]

## APPLICATIONS

### 1. Glass windows known to give energy efficiency

A window that has the capability of providing thermal comfort and illumination at very less demand of paid energy. This window will provide air conditioning in summers.

Overheating due to exorbitant solar input is troublesome. Energy efficiency can therefore be obtained by making use of glass windows coated with a thin film. Such windows are known as Heat Mirrors. They reflect the IR radiation and transmit the visible radiations. These windows have been created by making use of three layers on glass that is: Dielectric Metal Dielectric(DMD). This three layer thing serves as a highly reflective coating.

These windows incorporate a thin metal layer so as to reflect the IR spectrum of the solar radiation which we wish to block because of its excessive heating effects.

Silver has been used as the metal layer that is sandwiched between the dielectrics in this coating. This coated glass window has been proven to be very energy efficient. A temperature difference of 8°C has been noted between two glass window, one coated with this three layer system and one uncoated [14].

### 2. Highly Reflective Coatings for Micro scanning mirrors(MSM)

Micro scanning mirrors that find applications in NIR-VIS-UV regions of the spectrum have been developed by making use of highly reflective optical coatings.

Micro scanning mirrors have numerous applications ranging from spectroscopy, barcode reading, object identification and many others.

But in unprotected micro scanning mirrors that have an Aluminium coating, the maximum power density is being limited due to the heating induced by absorption. Therefore to give rise to new applications that require high power micro scanning mirrors (such as treatment of materials, large sized laser displays and laser marking) , highly reflective coatings are developed and studied.

In the NIR region of the spectrum, for applications that require high power MSMs, three different types of highly reflective coatings have been tested. The three types are:

- 1) Silver and Gold based metallic reflectors
- 2) Hybrid coatings
- 3) Multilayers with dielectrics

Studies have shown that the metal system shows high reflecting characteristics close to 98-99% at lower thickness of the coating that is 100-150 nm.

The hybrid highly reflective coatings have been tested and recommended for the application of micro scanning mirrors in the VIS and UV regions of the spectrum owing to the high reflectance that these coatings enable (up to 99.7%) but at a lesser thickness compared to the dielectric multilayers. In addition these hybrid coatings provide low stress and high mirror planarity[15].

### 3. HR Reflective coatings for projection screens

The commercially available projection screens today have a major drawback. Adequate contrast between the projected and ambient light is something that these screens are unable to give. Red, Green and Blue: these are the primary colors that are used for making the projected image in laser technology. This image formation is pixel by pixel just as that in a color television. If the light reflection by the screen happens only at wavelengths of these three primary colors of the projector, there will be a stark improvement in the contrast as the ambient light reflection will be greatly reduced. Thus highly

reflective (spectrally selective) coatings find application in laser display projection screens[16].

### 4. HR Coating for a Solar Receiver

In concentrating solar power, high-temperature sun powered receiver can give warmth to profoundly proficient cycles for electricity production. Unnecessary heating of the silica window followed by recrystallization are significant issues of high-temperature receivers utilizing windows.

By applying a reflective coating on the fused silica window inside, the exorbitant temperatures of the window can be avoided. The receiver and the glass temperature losses can both be reduced by using this coating which should be infrared reflective and solar transparent.

The coating has to be deposited on the fused silica window on the side that is opposite to the surface of the absorber. The fused silica substrate and the coating transmit the concentrated solar radiation which is then absorbed by the absorber. The coating should ideally transmit the entire radiation. It should also reflect most of the spectrum that is emitted by the absorber that is maintained at 1100°C back onto it[17].

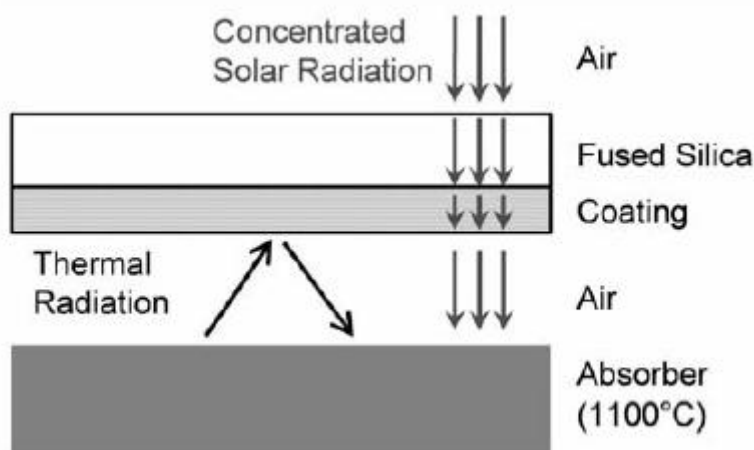


Fig 5.1: Operation principle of the coating[17]

### 5. BIOGRATINGS:

Biogratings are a comparatively new field of study and is emerging as an excellent area for measuring biointeractions quantitatively. Before the concept of biogratings is discussed, mentioning the concept of diffraction grating is important. A diffraction grating splits light into several beams, all of which travel in different directions. This optical instrument acts as a "super-prism". Spreading the wavelengths over a much larger angle than a prism, a diffraction grating will generally be used for measuring atomic spectra.

Biogratings are essentially diffractive gratings of bioreceptors and are made possible with the advances of nanoscience and nanotechnology. The use of diffraction based biosensing enables sensitive measurement of analytes and is an extremely resourceful tool in the food and pharmaceutical industry.

So how do these biogratings work? The biogratings consists of a highly reflective coating which comprise of active as well as deactivated binding reagent. In the absence of binding with its opposite member, there is no significant light diffraction. However, when the binding occurs, the coating creates a diffraction grating. This corresponds to the presence as well as the quantity of the analyte. Such biograting based biosensors find extensive applications in a wide array of fields from general healthcare monitoring to disease detection and even environmental pollution control.

Biogratings can be manufactured in several different ways. Usually, the reflective metal layers consist of aluminium, gold, chromium, titanium or nickel coating on a polished surface. An alternate reflective biograting comprises of multiple reflective layer units.



Immunoassay measures the presence of a macromolecule with the help of antibodies or antigens. Immunoassay systems require high sensitivity and it is for this reason that the highly sensitive biogratings came into being. The highly reflective biogratings combine high protein binding capacity and optical flatness to result in accurate measurements.

## 6. HIGH-REFLECTIVE COATINGS FOR SPACE BASED APPLICATIONS

Without the protective atmosphere that our earth provides, the need of highly reflective coatings in space bound applications becomes of paramount importance. Optical coatings have been extensively used in such applications since the beginning of space-borne missions. The coatings require a lot more study, detailing, tests and durability than the HR coatings used elsewhere. Testing in simulated space environments to test the several parameters are necessary. Be it the vacuum in the space, the debris floating around or the deathly radiations of the Van Allen Belt, highly reflective coatings for space bound applications must be equipped to deal with it all.

Coatings for space applications need to operate in environments from LEO (Low-Earth Orbit) to planetary and deep space probes. These environments provide dangerous radiation and thermal exposure which varies depending on the kind of space mission.

Highly reflective coatings are very important for space applications. Consider the LEO (low earth orbit) at an altitude of 400 km. This region contains the entire solar spectrum along with trapped protons and even solar flares. Located further we have the Global Positioning Satellites (GPS, 22,000 km) and High Earth Orbit (100,000 km). These regions carry vital optical instrumentation for climate monitoring, GPS services, military applications etc. If the radiation penetrates the spacecraft, it will alter the sensing measurements and can even drastically damage the sensing equipment. These radiations may interact with the spacecraft and produce an array of secondary particles, which again is danger sign. These problems are magnified when we have an astronaut in the spacecraft. Exposure to these plethora of radiations, trapped protons and the entire solar spectrum has proved to have damaging effects for the human body and there is a need to develop highly reflective coatings which can bear the severe environmental demands in order to advance a safe space research.

## 6. CONCLUSION

The review thus provides a deeper understanding on the working, types, synthesis and applications of highly reflective coatings. With the advances in nanoscience and nanotechnology, these highly reflective coatings are getting easier to manufacture and are providing a wide array of applications, not known before.

The paper tells us about the different types of highly reflective surfaces possible, the different ways for synthesizing them and also discusses the plethora of applications of the present

along with that of the future. Highly reflective coatings are necessary to reflect light not only in the VIS spectrum but also in the UV and IR regions. Silver is one of the most common reflective metal, however its durability provides challenges in the face of severe environmental conditions.

Metal coatings and Dielectric coatings are the two types of highly reflective materials which are considered. Metal nanoparticles have the ability to reflect light with a very high efficiency (eg. Silver). A graph of change in the reflecting properties of the metallic nanoparticles with change in the size is also shown in the paper. Dielectric coatings can offer reflectance values up to 99.9999%. In many scenarios, dielectric coatings are coated over metal nanoparticles to result in the highest possible efficiency.

The paper further discusses three different methods of synthesizing these highly reflective coatings. Each application requires a custom synthesis, and three broad categories are discussed, namely: Sol-gel method of  $ZrO_2$ - $SiO_2$  derived HR coatings, highly reflective metal coatings of silver nanoparticles by assembling in polymer matrix and Hybrid HR coatings (Inorganic + Organic compounds).

The last section of the paper tells us about the several applications of highly reflective coatings and how research in these areas are leading to new and exciting possibilities. Be it energy efficient glass windows, biogratings or applications for space missions, the use of highly reflective coatings is much needed and its value is going to increase over the course of time propelling further research in these areas and leading to newer discoveries and simpler, yet cheaper methods of synthesis.

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