Optical properties and applications of nano-structured oxide thin films

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Overview

Metal oxides are the preferred materials for fabrication of many optical coatings for the UV, visible and near infrared. Optical interference occurs in thin films with thicknesses of the order of the wavelength of light, and such coatings form the basis as building blocks for many multilayer optical coatings.

Multilayer films with individual thicknesses of only a few nanometres can exhibit interesting optical and mechanical properties, features that can be exploited in the design and manufacture of precision optical coatings. This presentation explores some current optical applications, describes some results and discusses the observations.
Nano-structured thin films

- Nano-structured materials are defined as functional materials having features such as layer thickness of a few nanometres thick.
- Multilayer films with individual thicknesses of only a few nanometres can exhibit interesting properties.
- For example, it is well known that multilayer coatings for machine cutting tools have produced hardness and toughness exceeding that of the constituent materials, thereby increasing wear resistance.
- In metallic / ceramic coatings for wear improvement it has been shown that the Vickers hardness of the composite material can be up to 3 times greater than the individual materials.
- The reasons are not fully understood and several models have been proposed.
- We will explore how nanostructured coatings fabricated from metal oxides can be developed for optical applications.
Optical thin films - background

- Optical thin films modify the way light is transmitted through (or reflected from) a transparent surface by a phenomenon known as ‘interference’.

- The colourful patterns in soap bubbles and oil films are due to interference effects caused by multiple reflections from the surfaces of the film.

- Optical thin film design encapsulates this principle in solid form where layers of different transparent materials are deposited onto a substrate to a predetermined design thickness.
**Thin film designs**

- Multiple reflections at layer interfaces causes interference effects, enhancing some wavelength, suppressing others.

- Optical thin film coatings typically rely on the difference in refractive index of two or more transparent materials to produce interference effects that modify the transmission and reflection spectra of optical components.

- Metal oxide materials such as TiO2, HfO2, SiO2 are routinely used in the design of filters and antireflection coatings.
**Thin film design: reflector**

- Alternating high and low index layers (high low quarter-wave stack) will produce a reflector at a wavelength where the optical thickness of each layer is a quarter wavelength.

- Using alternate layers of TiO2 and SiO2, a typical transmission spectrum of a reflector is shown below.
Reflector refractive index profile

Refractive index profile of alternating high index (TiO2) and low index layers (SiO2) plotted against coating thickness. This is a square wave refractive index profile.
Thin film design: reflector

- On the short wavelength side of the reflector, reflection bands occur at wavelengths where the layer thickness are odd multiples of the quarterwave stack.

- At wavelengths corresponding to approximately $1/3^{rd}$ and $1/5$th of the reflector wavelength, reflection bands occur (these are at harmonic frequencies).
Alternative designs of optical coatings

• Where suppression of harmonic stop bands is important, and alternative design strategy is required.

• A sine wave has no harmonics, so it is useful to consider what the spectrum would look like where the refractive index varies in a smooth sinusoidal way from high to low index, rather than a step change.

![Refractive index with thickness](image.png)
Conventional design and graded index design

Continuously variable refractive index designs are termed graded index. Although the concept is well known, the design and manufacture can be implemented in different ways, and we will look at one such way in more detail.
Graded index optical coatings

The continuous sine wave can be approximated by index “steps” that follow the basic sine wave profile as shown below. The spectral transmission is plotted in the next slide:
Graded index optical coatings

The spectral transmission of the “stepped” index design is shown below. Although there are many ripples, note the lack of short wavelength harmonic reflection bands.
**Graded index optical coatings**

The difficulty is that this relies on several materials of different refractive indices, materials which may not be available in practice, or have incompatible properties with each other. This can be resolved in two ways:

- Co-deposition of high and low index materials
- Simulate the intermediate index materials by very thin layers of high and low index materials in the appropriate proportions

Co-deposition can work very well but demands very accurate control of proportions of high and low index materials. This best achieved by reactive magnetron sputtering of silicon in a mixed oxygen nitrogen atmosphere.

We are concentrating on the second way, “frequency modulated digitising”
Graded index optical coatings

An example of a digitised graded index shortpass filter with matching layers to minimise pass band ripple. The spectral transmission shows absence of reflection harmonics. The design uses real dispersive materials of TiO2 and SiO2.
Graded index designs and rugate filters

• Coatings where the refractive varies in a periodic and repetitive way are called rugate, from the Latin “rugatus” meaning crinkled or wrinkly. Rugate technology is a thin film design concept that has been around for about two decades.

• This technique originally developed for the design of very narrow stop-band filters is a concept where spectral properties are derived by the refractive index modulation of a material rather than discrete thick layers.

• The resultant refractive index modulation can be digitised into discrete very thin layers in the same way as analogue signals can be converted into digital information.

• The higher the digitisation, the more accurate is the resolution of the original desired spectral profile.

• The resultant digitised design have layer thickness of the same order as nano-structured films.
Typical rugate spectrum and digitised refractive index profile

Digitised refractive index profile
Advantages and applications

Graded index and rugate design are powerful design techniques which can be used where conventional designs fail. Although the layer thickness are much thinner than conventional designs and the layer count very high, they are used in a number of applications. Examples of these are:

- Laser protection filters
- Antireflection coatings
- Multiple notch laser rejection filters
- HUD combiners
- Graded Head-Up Display coatings

Our sister company, Orion Photonics Ltd uses this strategy for a number of applications, the manufacture of which is discussed later.
Advantages and applications

Laser protection filters are designed to suppress a narrow wavelength laser and transmit the rest of the visible spectrum. Digitised rugate designs can be used for such applications. The example below is the measured transmission.
Rugate antireflection coating

Example of a antireflection coating using rugate design principles using very thin TiO2 and SiO2 layers (theoretical design).
Single notch Head-up display combiner

Monochromatic HUD displays need only a single notch rugate combiner coating to maximise outside world transmission and display brightness simultaneously. The notch wavelength and depth can be optimised from design eye position so that the display appears uniformly bright.
Head-up display combiners

We have shown the spectrum of a single sine wave. By superimposing different sine waves and generating a complex refractive index profile, multiple notch rugate filters can be designed with each notch tuned to a different wavelengths, typically reflecting blue, green and red wavelengths.

Display at 470nm, 532nm and 640nm
Photopic transmission 81.9%
Chromaticity: x = 0.310, y = 0.326
Graded Head-up display combiners

• In fighter aircraft where space is limited, most military head-up displays use two combiner plates at an inclined angle, parallel to each other but separated vertically to increase field of view.

• The reflected image is therefore ‘shared’ between the upper and lower combiner and it is important that in this configuration, the pilot’s view of the outside world is clear with no discontinuities.

• To facilitate this illusion, the combiners overlap each other, and in the overlap region, the image reflected by each combiner plate is progressively reduced (or feathered) to make the transition of the image between each combiner smooth, and the combiner edges almost invisible. The overlap region in the dual combiner assembly is called the ‘grade’.
Graded Head-up display combiners

Rugate technology enables this by varying the effective index amplitude across the surface of a combiner plate, the coating can be a narrow reflective notch in one area with the notch progressively reducing until it becomes an antireflection coating in a different area. The graph below shows this effect.
Manufacturing constraints

• Unlike conventional designs, graded index coatings require very many layers with thickness of a few nanometres to a few tens of nanometres which is over an order of magnitude less than conventional films

• The manufacturing process must be very accurate with tight control in refractive index and thickness accuracy

• Conventional single point optical monitor techniques are inappropriate due to the small change in optical signal

• There is a need to be aware of potential interface effects at layer boundaries.

• We have found that plasma assisted deposition overcomes many of these problems
Plasma assisted coatings

• The advent of ion assisted and plasma assisted deposition techniques provided a major advance in thin film properties.

• In this technology a source of energetic argon and/or oxygen ions are generated under vacuum and directed at the substrate during the deposition process.

• Plasma assisted processes provides the growing film with enough surface mobility to make the films amorphous, with densities close to that of the bulk material, and films virtually free of voids.

• The process allows excellent control of layer thickness and refractive index, a prerequisite for very thin films.
Manufacture and environmental properties

- Plasma assisted deposition of metal oxides of TiO₂, HfO₂ and SiO₂ together with tight control of all process parameters has enabled digitised graded index designs to be manufactured routinely.

- The process control and stability of refractive index enables the accurate deposition of coatings where layer thickness is on a nanometre scale.

- The lack of voids within the thin films means that the coatings are spectrally stable over a wide range of temperature and humidity environments.

- The films are very robust
Mechanical properties of nano-structured coatings

It might be thought that optical coatings with up to several hundred thin layers might exhibit poor environmental properties compared with conventional designs. In our experience, this is not the case and there is evidence that nano-structured optical filters provide better environmental performance than conventional coatings.

• It has been reported that rugate filters have superior abrasion resistance and humidity performance than conventional thin films.

• It has been demonstrated that rugate coatings on polymer substrates are less prone to delamination than conventional coatings.

• Compressive stress of the coatings is less with rugate designs than with conventional designs of similar physical thickness.
Possible explanations of the hardness of nano-structured coatings

With metal / ceramic coatings for wear improvements to machine tools, the reasons are not fully understood and several models have been proposed:

- One model is based on dislocation motion within layers and across layer interfaces, causing migration of defects away from layer interfaces.
- The principle is sometimes called supermodulus effect.
- Nano-structured optical thin film coatings may have similar properties to some degree.
Summary

• Graded index coatings offer thin film optical designs which are difficult or impossible to design using conventional design techniques.

• Using index steps and digitising the graded index design results in coatings with very many thin films with layer thickness approaching nanostructures.

• Although digitised graded index designs and rugate coatings can have large numbers of very thin layers, manufacture using plasma assisted electron beam deposition overcomes many inherent problems.

• There is evidence to suggest that such structures can have excellent mechanical properties and reduced stress.