Topic area: **CMMSP**

Crystallinity in Lumogen Optical Thin Films

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Introduction

Lumogen Yellow S is a commercial pigment material with fluorescent properties that facilitates its use for wavelength-converting optical coatings. A common application is in ultra-violet downconversion, as it absorbs radiation in the ultraviolet and re-emits at visible wavelengths. Due to its very high conversion efficiency, lumogen films are used to increase the quantum efficiency (QE) of silicon-based photon detectors such as charge coupled devices (CCDs) [1]. To further illustrate this application, Lumogen Yellow coatings have been used in the UV imaging systems of the Hubble Space Telescope [2] and the Cassini-Huygens Spacecraft that reached the Saturnian system in 2004.

Lumogen coatings are considered very stable, however previous reports have shown that as-deposited amorphous Lumogen films exhibit non-uniformity [3], and crystalline growth within the film, if left standing at room temperature for a length of time [2,4]. These properties influence the optical properties and hence affect the performance of these films. In this research area, we are interested in harnessing this behaviour to produce nanocrystalline coatings with controlled optical properties.

Using a physical vapour deposition method (PVD) under vacuum, commercial Lumogen® Yellow S 0790 [5], an azomethine based pigment material with chemical structure as shown in figure 1(a), was deposited on flat silicon dioxide glass slide surfaces.

The film structure has been studied using a range of techniques such as X-ray Diffraction (XRD), Ultraviolet-Visible Absorption Spectroscopy (UV-vis) and Scanning Electron Microscopy (SEM) and show evidence for crystalline structures within the film. In this paper, we aim to demonstrate the formation of crystalline structures and that there is a significant influence of the storage temperature upon the nucleation and growth rate of crystals within the film.

Results

The optical properties of Lumogen coatings are best characterised by UV-vis absorption spectra. Figure 1(b) shows the absorption spectrum for a lumogen film, as deposited by PVD under vacuum onto a room temperature substrate. This data is comparable with that reported previously by Deeg and Ninkov [6] and is characterised by a number of distinctly identifiable excitation modes. Considering that the emission band ranges between 500 and 650nm [4], lumogen is clearly an ideal down converting material for UV detection by devices that are efficient at detecting visible wavelengths.

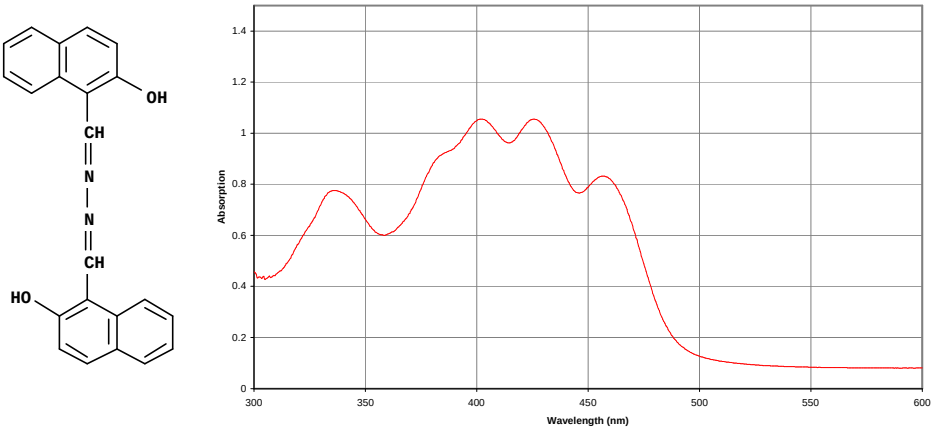

Figure 1. *(a) The chemical structure of Lumogen® Yellow S 0790. (b) UV-vis absorption spectrum of a Lumogen Yellow S 0790 film, deposited onto a room temperature substrate. Note that the emission spectrum of lumogen ranges from 500 to 650 nm [4].*

To study the presence of crystalline structures within the film, X-ray diffraction (XRD) was used. Since XRD spectra indicate changes in crystal structure and development, samples were subjected to a post-deposition annealing treatment at 80^{o}C in an oven under atmospheric conditions.

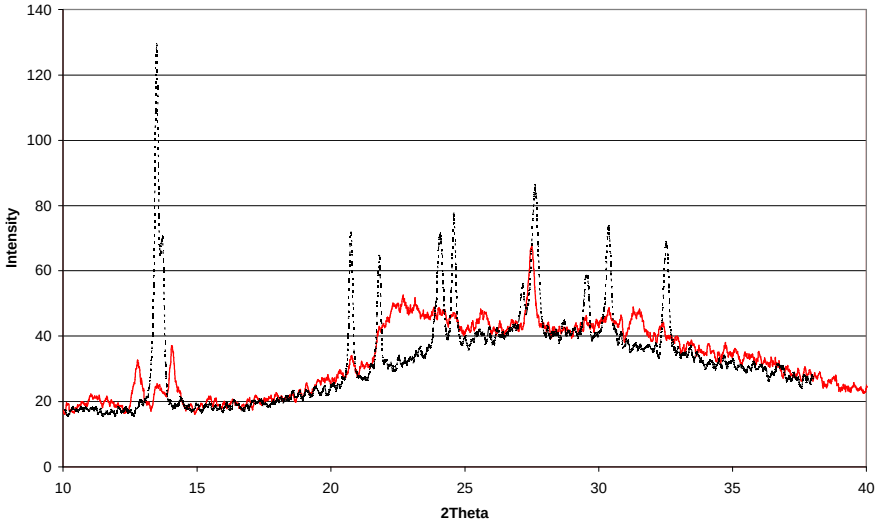

Figure 2. *An XRD scan of a Lumogen Yellow S 0790 film deposited at room temperature (solid line) and then after being annealed at 80^{o}C for approximately 88 hours(dashed line).*

The XRD scan of the untreated (as-deposited) film, shown as the solid line spectrum in figure 2, exhibits features that are commonly observed in our films. After annealing, the XRD spectrum is observed to change dramatically, with the emergence of several peaks, clearly indicating the development of increased crystallinity within the film.

XRD results for different periods of treatment were obtained and indicated dramatic changes in film characteristics. XRD studies of coatings stored under ambient conditions also indicate change in the film structure post-deposition over longer periods (weeks or months).

The development of crystallinity within the film was confirmed by SEM imaging. Figure 3 shows an SEM image illustrating the typical elongated planer crystal structures that develop. Similar 'sheet and stack' structures form in perylene based dye crystals [7] which are the basis of lumogen F dyes.

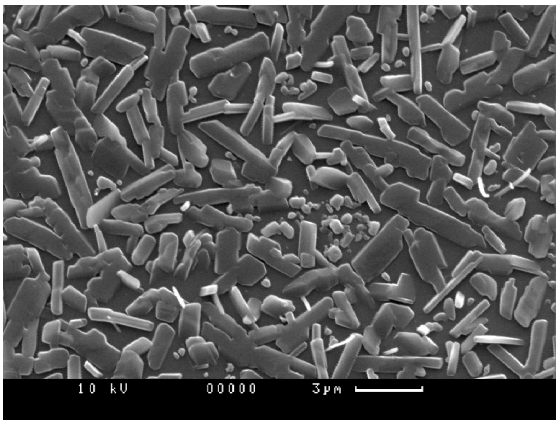

Figure 3. *SEM image of a thin film of Lumogen® Yellow S 0790 deposited on a silicon dioxide slide. The substrate is evident between the developing crystals.*

Depending upon the substrate temperature during the deposition process, initially the film deposits relatively uniformly, but the material then nucleates into small semi-symmetric crystals with a characteristic dimension of a few hundred nanometers. An example of such nano-crystals is evident near the centre of the SEM image in figure 3. The energetics are such that crystal growth results in planar structures with a propensity to develop in one dimension resulting in large aspect ratio crystals with typical lengths of ≈3-4 μm for a range of deposition conditions. Detailed correlation of SEM and XRD results for a range of deposition and treatment conditions is continuing at present.

The comparison of UV-vis absorption spectra with the XRD results of the same samples gives an indication of the subsequent change in optical properties of the films that result from structural changes. UV-vis absorption and XRD spectra were taken for a thin film (with an estimated thickness of 100-200 nm) deposited on a room temperature substrate. The sample was subsequently heat treated for 1 hour, and re-scanned. This process was repeated for several time periods to study the kinetics of crystal growth. The dashed line in Figure 4 shows the dramatic variation in UV-vis spectra after only 1 hour of heat treatment. It is proposed that the apparent significant increase in absorbance that is evident for wavelengths greater than 500 nm is due to the reconstruction of the film surface. The initially deposited film is relatively uniform and the spectrum represents the absorption by the material of wavelengths less than 500 nm which occurs across the entire sample surface. With modest thermal treatment, the bulk of the 'film' thins as it utilises material to form 3D crystals on the surface, which would result in a decrease in absorbance. However, this may be offset by diffuse scattering from these crystals at a continuous range of wavelengths, resulting in a loss of intensity being detected over the entire wavelength range.

Further heat treatment results in further crystal growth, hence thinning the film further and resulting in less contribution from the absorption by the material and more from the diffuse scattering by the developed crystals now forming a textured surface layer. This model is also consistent with the XRD results, which show rapid development of peaks (see figure 2) for short periods of heat treatment and subsequent small adjustments.

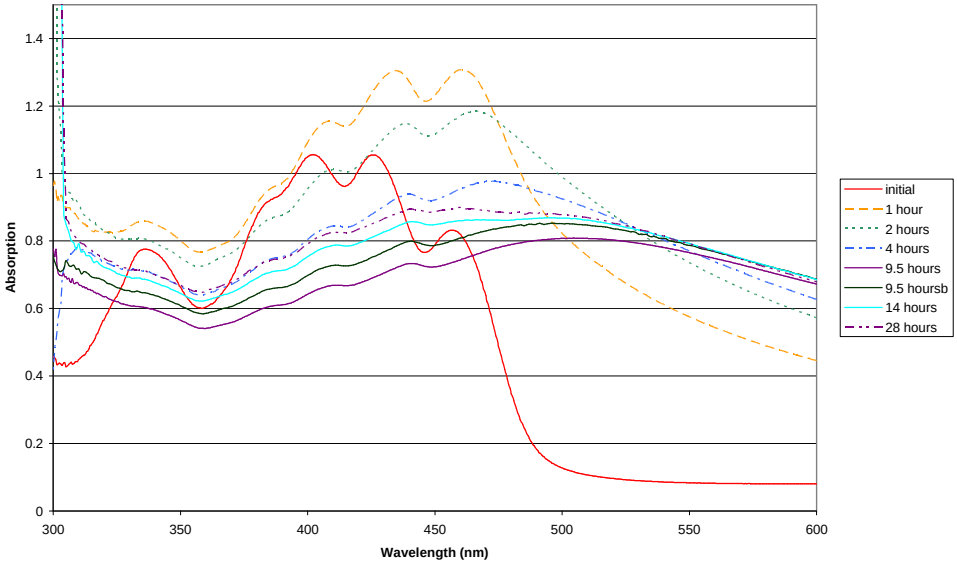

Figure 4. *Changes in the absorption spectrum of Lumogen coating after annealing at 80°C for various time periods. The initial spectrum represents the absorption for a thin film deposited on a room temperature substrate. Note the dramatic increase in absorption at longer wavelengths after only a short period of annealing. .*

Summary

Crystalline structures within thin Lumogen Yellow S optical films have been observed to vary as a function of time, particularly if exposed to an elevated temperature. The film structure has been studied using a range of techniques such as X-ray Diffraction (XRD), Ultraviolet-Visible Absorption Spectroscopy (UV-vis) and Scanning Electron Microscopy (SEM). Comparison between UV-vis spectra and XRD results indicates the influence of film structure and morphology upon the resultant optical properties of the film.

Studies of the dynamics of crystal development at early times for a range of energetics and interpretation of the XRD spectra are ongoing. Investigation into the structural changes of these films and subsequent changes in their optical properties will enable films to be produced with maximum stability and uniformity. In future, the ability to tailor the optical properties of these coatings may enable superior detector technologies.

References

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