The Research of Ultraviolet Detection by using CCD

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ABSTRACT

Lumogen Yellow S 0790 is a commercial pigment based on azomethine and is used for enhancing charge-coupled device (CCD) for detecting ultraviolet radiation. It's used as a wavelength up-shifter, whereby short wavelength ultraviolet (UV) light that is absorbed by the material is rapidly re-emitted with longer wavelengths in the visible spectra, for improving the spectral response of CCD detectors. In this work we research on differences of the crystallized sample and the re-crystallized sample in crystal structure, morphology and optical properties, including laser-induced fluorescence excitation spectrum, emission spectrum and Raman spectra. The results show that re-crystallized Lumogen sample has better crystalline structure on the application of ultraviolet sensitizer. By using the re-crystallized as-deposited Lumogen films on glass substrate in front of the CCD detector, ultraviolet can be detected and quantized better.

Keywords: PVD, Lumogen, Up-shifter, CCD, Crystalinity

1. INTRODUCTION

Lumogen Yellow S 0790 is a commercial pigment based on azomethine and is used for enhancing charge-coupled device (CCD) for detecting ultraviolet radiation. It's used as a wavelength up-shifter, whereby short wavelength ultraviolet (UV) light that is absorbed by the material is rapidly re-emitted with longer wavelengths in the visible spectrum, for improving the spectral response of CCD detectors. Many of the features which make Lumogen desirable for this application (low boiling point for ease of deposition, high conversion efficiency, and short decay time) are a result of its organic nature. Under a normal condition, Lumogen Yellow S 0790 is a kind of yellow powder, which is nontoxic and not dissolve in water or alcohol, and it is been proved that it has stable chemical properties in previously research. The chemical structure of Lumogen, or 2-hydroxy-[(2-hydroxy-1-naphthalenyl) methylene] hydrazone[1], which comprises an hydroxyl terminated naphthalene group attached to each end of an azomethine chain, is shown in figure 1.

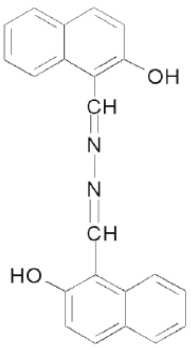

Fig. 1. The chemical structure of Lumogen Yellow S 0790.

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Employment of a thin, translucent Lumogen film on the front side of the CCD enhances the UV response of the device, but a small penalty is paid in the visible region due to attenuation by the overlayer film. Besides thickness, another factors which effect the spectrum are the size and shape of crystalloid of Lumogen.

The conversion efficiency of Lumogen films can be estimated by evaluating their performance on CCDs. The emission peak of Lumogen is at 530nm. The quantum efficiency of a front side CCD at this wavelength is about 30%. If the Lumogen film had a conversion efficiency of 100%, the UV quantum efficiency of a Lumogen coated CCD would be 15% because the emitted light is randomly directed. Actual QE in the UV is about 12% to 13%, yielding a conversion factor of better than 80% for the Lumogen films.[2]

For stability, previous research shows the Lumogen films appear to be stable against relatively intense UV radiation, the vapor pressure of Lumogen at 95°C is large enough that voids occur after short times under high vacuum conditions. [3]

In this work we compare the crystallized sample and the re-crystallized sample in crystal structure, morphology, laser-induced fluorescence excitation spectrum, emission spectrum and Raman spectra. The results show that re-crystallized Lumogen sample has better crystalline structure on the application of ultraviolet sensitizer.

2. EXPERIMENTAL

Physical Vapour Deposition (PVD) method has been widely used in the production of crystalline Lumongen, the previous literatures have studied the morphology and optical properties of Lumongen.[2] However, crystallization Lumongen sample have been re-sublimated and re-crystallized, which will be not shown the same morphology and optical properties. In this work, crystallized and re-crystallized crystalline Lumongen samples produced by PVD method are compared with microscope, Raman spectrometer, as well as other test equipment.

2.1 AS-DEPOSIT LUMOGEN FILM ON GLASS SUBSTRATE

In this work, PVD was employed to deposit the Lumogen coatings on flat glass substrate (which has been cleaned) in a vacuum container in case of oxidation in high temperature. The bottom of the vacuum container is heated by a solder-pot.

First, we take a very small stock of powder into the container at the bottom, and glass substrate was hung on the lid of the container with steel wire. Then carefully close the lid and lock it. Hence the sealed vacuum container was completed.

The second step is to connect the vacuum container with a vacuum pump, and open the valve of the container. Be sure that the entire container is in well-sealed, open vacuum pump, pumping the air. Then close the valve, disconnect the connection with the vacuum pump. In this way, the container to gain a degree of vacuum to ensure that the heating in the subsequent steps will not cause the Lumogen powder to be oxidized.

The next step is heating step, also the key step of the whole processing, this step's purpose is to enable Lumengon sublimate by heating in vacuum environment, and turn into steam to be full of container. Because the heating of solder-pot is carried out under the bottom, so the upper half of the vacuum container has lower temperature than the lower half, so that steam will deposit symmetrically on the glass substrate which near the top of the container (because of the vacuum of the container, It's hard to conduct the heat to the glass substrate). Let solder-pot turn on, the Lumongen powder in the bottom of the container will be sublimated (temperature higher than the sublimation temperature 328.6°C). After that, turn off the solder-pot, remove the vacuum container and cooling it by fan. Waiting for the temperature falling down until near to room temperature, open the valve and the lid, finally we can take out the as-deposit Lumogen film.

2.2 THE RE-CRYSTALLIZED LUMOGEN FILM

As we can see on the glass substrate, Lumogen steam crystallized on the glass as well as the inner surface of the vacuum container (most of them cling on the upper area). After that change a new glass substrate and repeat the former process without any new Lumogen powder added in the container, so that the crystallized Lumogen on the inner surface could sublimate again and re-crystallized on the new glass substrate, this is how we make re-crystallized as-deposit Lumogen film, the photo of it is in figure 2.

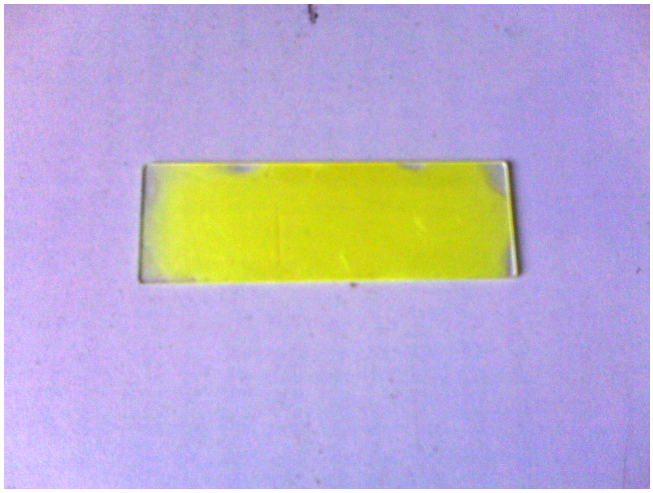

Fig. 2. The re-crystallized as-deposit Lumogen film on glass substrate

3. RESULTS

3.1 CRYSTAL STRUCTURE AND MORPHOLOGY

The crystallized and re-crystallized as-deposit Lumogen film we got in previous experiments are taken under a 500X optical microscope, we can see their surface morphology structure in figure 3 and figure 4 below.

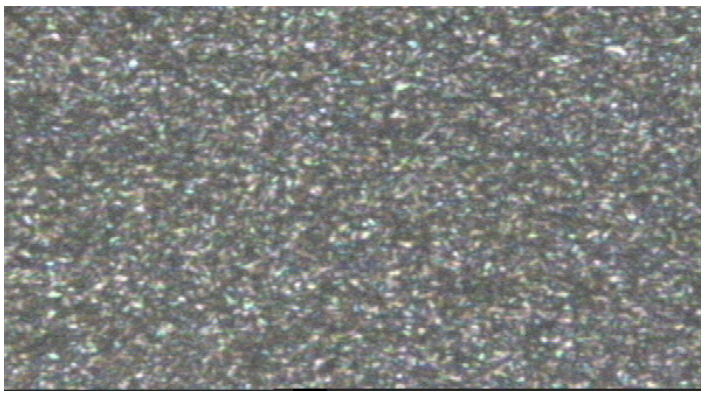

Fig. 3. The surface morphology structure of crystallized sample

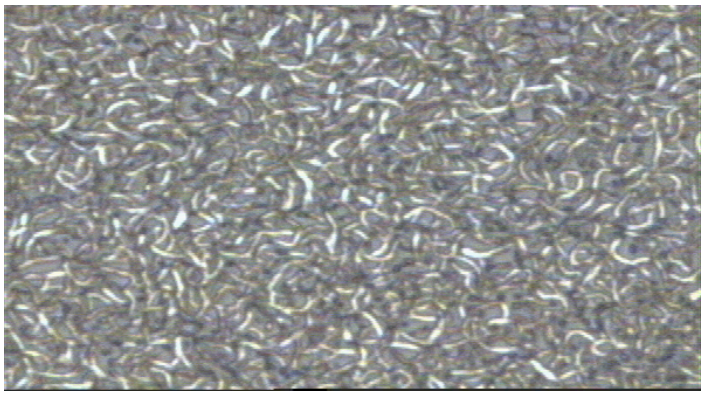

Fig. 4. The surface morphology structure of re-crystallized sample

A dramatic change in crystal morphology is observed, by contrast the above picture it is clear that re-crystallized Lumogen samples has bigger crystal than the first crystallized Lumogen samples, such a clear distinction between the form is bound to lead to the difference in crystal structure, which makes the difference in the optical properties (to be discussed later).

3.2 LASER-INDUCED FLUORESCENCE EXCITATION SPECTRUM

In the excitation spectrum experiment, we test the light-emitting efficiency (quantum efficiency)[4] of crystallized and re-crystallized as-deposit Lumogen film in 530nm and 570nm emission light with different wavelength excitation light. Mapping the light-emitting efficiency changes with the wavelength is the excitation spectrum. We selected 530nm and 570nm emission light to engage in the experiment, because the two bands show strong fluorescence emission in the emission experiment (we will discuss it later). In the excitation spectrum experiment, we put the data curves of crystallized and re-crystallized sample in one image to compare, it is noteworthy that the data has been normalized, so the intensity (ordinate) are relative values, it only can manifest the trends of response to the different wavelength emission light of the two samples, As shown in figure 5 and figure 6.

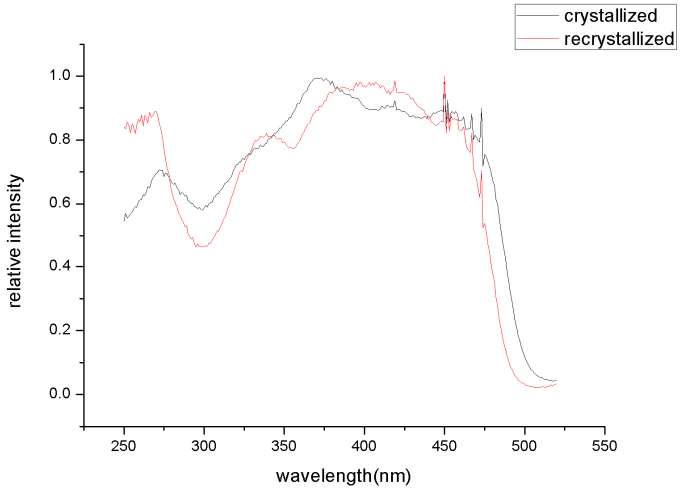

Fig. 5. Excitation spectrum: the comparison in 530nm

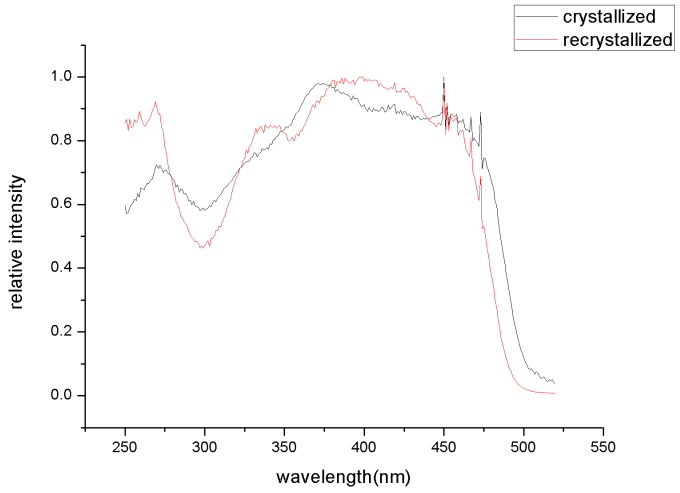

Fig. 6. Excitation spectrum: the comparison in 570nm

Through contrast the image above, we can obviously find out that there is a general trend in all curves: when the wavelength of excitation light is between 250nm and 280nm, shows a corresponding good efficiency, and then the efficiency decrease rapidly to reach a minimum at about 300nm, followed by a upgrade, then perform at their best in the vicinity of 400nm, and continued until 450nm, when the excitation wavelength over 470nm, the light-emitting efficiency of the samples decreased rapidly, if the excitation light in 500nm around, there has been unable to obtain any fluorescence.

If we examine the re-crystallized sample curve (red line in figure 5 and figure 6) and the crystallized sample curve (black line in figure 5 and figure 6) in each image carefully, we would notice that the re-crystallized sample curve shows more response in 250nm ~ 270nm band and 400nm ~ 450nm band. Of particular note is that both in the 530nm result and the 570nm result, the re-crystallized sample have an obvious wave crest around 340nm, which is not appear in crystallized sample result.

The crystal structure of re-crystallized sample and crystallized sample cause the differences in shape and size, which further lead to their differences in optical properties. Re-crystallized sample has greater Lumogen crystal, and more sensitive in UV-C band (UV under 290nm). In practical applications, we are able to take advantage of this characteristic, by using re-crystallized Lumogen in sensitized UV detection, can achieve better results for short-wavelength ultraviolet light.

3.3 LASER-INDUCED FLUORESCENCE EMISSION SPECTRUM

In the emission spectrum experiment, we test the relative intensity of fluorescence of re-crystallized sample and crystallized sample in the 400nm excitation light wavelength circumstances, and map the relative intensity of fluorescence changing with the fluorescence wavelength into a curve, that is, emission spectrum. Because the excitation spectrum in the previous experiment shows that both the two samples have a good response in the 400nm area, we chose the 400nm wavelength as the excitation light, and the same as excitation spectrum experiment, the data has been normalized and the ordinate is only relative intensity. The figure is shown as follow.

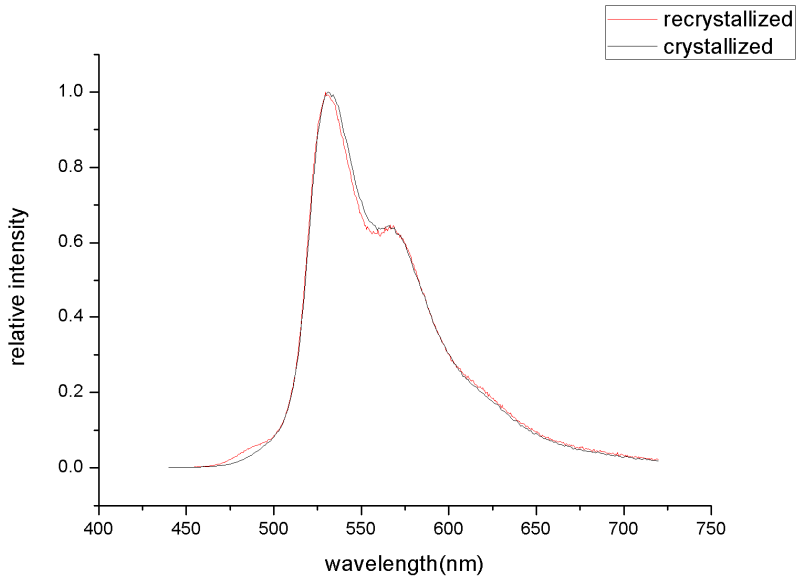

Fig 7. Emission spectrum: the comparison in 400nm

The two lines in the image both have two peaks nearby 530nm and 570nm, this is why we use these two wavelength as emission light in previous excitation spectrum experiments. This result is cross-checked against the results in excitation spectrum experiments, shows that it's correct of the wavelength choice. [5]

The difference between emission spectrums of re-crystallized sample and crystallized sample is very small, two lines in the image are nearly the same, the only difference is re-crystallized sample has a extra wave crest in 480nm around. It's hard to explain what makes this small wave crest, no research in previous mention this feature, we suppose it's the influence of the bigger crystal size.

Through the emission spectrum experiment we can see that if the violet light of 400nm wavelength through Lumogen film, it can transform to yellow and green light, combine with the results in the excitation spectrum experiment before, we can infer that the UV light can be converted into visible yellow and green light after it pass through Lumogen film, which can be detected by CCD.

3.4 RAMAN SPECTRA

In following Raman Spectra experiments, we test the Raman spectra of re-crystallized sample and crystallized sample. The test results are shown as in figure 8 and figure 9 below, it is noteworthy that from the previous test results we can be aware that the fluorescence spectrum of the two samples in the same band is not exactly the same, so in the Raman spectra, the fluorescence signal in the context is not comparable, we only need to observe the results of comparing the results of the Raman spectra and ignore the background fluorescence signal. The results are shown in following figures.

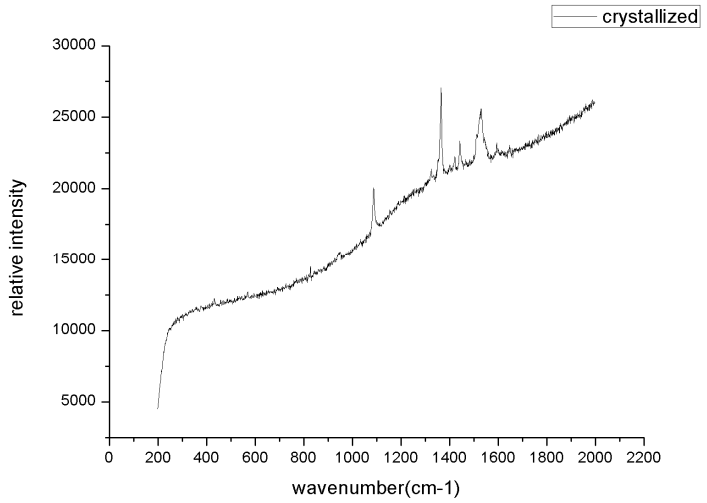

Fig. 8. Raman spectra of crystallized sample

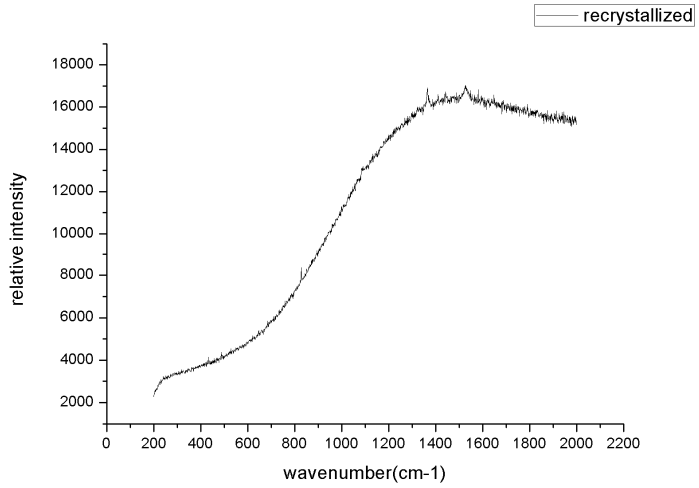

Fig. 9. Raman spectra of re-crystallized sample

Compare the two Raman spectra above, we can clearly indicate the peaks in wave number of 830, 1350, 1450 and 1550, they have shown a certain intensity of Raman spectra, the Raman spectra of the two samples appear essentially in the same position of the spectrum. There are two main differences between them: first, in general the crystallized sample has much more strong Raman spectra intensity than the re-crystallized sample; second, it's easy to find out there is one more extra peak in the Raman spectra of crystallized sample in the wave number 1100 which is not shown in the re-crystallized sample. This phenomena may be due to generally more weak Raman spectra of the re-crystallized sample, in that case, this peak which should be there might be too weak to distinguish, or it may because there has no peak here in the Raman spectra of the re-crystallized sample at all, in other words the crystal structure difference between the two samples led to the disappearance of the peak here.

4. CONCLUSIONS

Crystallized and re-crystallized Lumogen Yellow S 0790 films are made by PVD, and a series experiments including laser-induced fluorescence excitation spectrum, emission spectrum and Raman spectra are taken to compare the difference in optical properties of them. Clear differences are shown under microscope that the crystallized molecule and re-crystallized molecule are not the same in size and shape. Laser-induced fluorescence excitation spectrum comparison shows that the re-crystallized sample has better response in UV-C. The different Raman spectra in $1100cm^{-1}$ also verify the difference. These results mean that re-crystallized Lumogen has better crystalline structure on the application of ultraviolet sensitizer. By using the re-crystallized as-deposited Lumogen films with glass substrate in front of the CCD detector, ultraviolet can be detected and quantized better.

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