Current Optics and Photonics
Vol. 1, No. 4, August 2017, pp. 284-288

ISSN: 2508-7266(Print) / ISSN: 2508-7274(Online)
DOI: https://doi.org/10.3807/COPP.2017.1.4.284

Thickness Dependence of Ultraviolet-excited Photoluminescence Efficiency of Lumogen Film Coated on Charge-coupled Device

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(Received February 23, 2017 : revised July 10, 2017 : accepted July 10, 2017)

In order to investigate the ultraviolet-excited photoluminescence properties of phosphor coatings and their relationship to thickness, Lumogen coatings with different thicknesses were deposited on quartz substrates and charge-coupled device chips by thermal evaporation. The variation of the film thickness affected the crystallite size, surface roughness and fluorescence signal. It was found that the Lumogen coating with the thickness of 420 nm has the largest luminescent signal and conversion efficiency, and the corresponding coated charge-coupled devices had the maximum quantum efficiency in the ultraviolet. These results provided one key parameter for improving the sensitivity of Lumogen coated charge-coupled devices to ultraviolet light.

Keywords : Photoluminescence, Film thickness, Phosphor coating, Ultraviolet light
OCIS codes : (040.5160) Photodetectors; (040.7190) Ultraviolet; (160.2540) Fluorescent and luminescent materials; (300.6280) Spectroscopy, fluorescence and luminescence

I. INTRODUCTION

Silicon-based photodetectors with broadband spectral response, especially array devices of charge-coupled devices (CCD) and complementary metal oxide semiconductor (CMOS), have great desirable applications in spectrometer and space imaging, due to their reliability and compactness. However, the present CCDs have low quantum efficiency (QE) at Ultraviolet (UV) and deep Ultraviolet (DUV) wavelengths compared with that at visible wavelengths due to the absorption of the electronic gate structure deposited on the front or on the silicon substrate [1, 2]. Even though the thinning and back illuminated technique for UV responsive CCD can reduce the absorption loss of UV light, the high cost and difficulty in fabrication are still disadvantages in their applications in the various instruments [3]. It is possible to make CCD sensitive to UV light by simply incorporating a phosphor coating on the front-side of the CCD chip, which absorbs UV photons and re-radiates in the visible [4-11]. There are some kinds of fluorescent material for UV-responsive CCD [12-15] and solar cell efficiency enhancement [16]. There are also many demands for higher sensitivity of UV CCD for weak signal detection, such as fingerprint recognition and trace analysis. Essentially, the conversion efficiency and life expectancy of fluorescent coating films are determined by many factors [17, 18], such as crystal morphology, scattering and self-absorption, contaminants in the film, reflection at the air/film and other interfaces, etc. Thus, the parameters of phosphor coating need to be studied for sensitivity enhancement of the phosphor-coated device. It is worthwhile to consider the properties of fluorescent coatings prepared by a thermal evaporation method in the vacuum system as a function of thickness. In this paper, we fabricated a series of Lumogen films deposited by thermal evaporation on the quartz glass substrate and CCD, and discussed the influences of the

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thickness on fluorescence and conversion efficiency of Lumogen thin films as well as the quantum efficiency of the corresponding CCDs. Finally, we obtained the optimum thickness of the film.

II. EXPERIMENT

Phosphor coatings (Lumogen S0795, BASF) were deposited on the quartz substrates and charge-coupled device chips by thermal evaporation at room temperature. Prior to position in the deposition system, glass substrate slides were rinsed in acetone, ethanol and distilled water sequentially. Lumogen powder was packed into a molybdenum boat. The chamber was pumped to an ultimate vacuum pressure of 8×10^{-4} Pa before deposition. The deposition rate of 0.5 nm/s and the thickness for all films were monitored during deposition by using a quartz crystal monitor (SQC-310, INFICON).

The crystal structures of the films were characterized by X-ray diffraction analysis (D8, Bruker). The data for phase identification was collected in a 2θ range from 10 to 60°. The surface morphology was measured by atomic force microscopy (XE-100, Park). The photoluminescence spectrum was acquired by a fluorescence spectrometer (Dual UV-NIR, Horiba). The conversion efficiency was obtained by a spectrophotometer with integrating sphere. The thickness of Lumogen thin films was measured by a stylus profilometer (XP-1, Ambios). The QE of CCD chips coated with Lumogen film was measured by a CCD & CMOS characterization system (MV-IS-2011, Enli). All the measurements were carried out at room temperature.

III. RESULTS AND DISCUSSIONS

X-ray diffractograms of the Lumogen films with different thickness are shown in Fig. 1. All films have two characteristic peaks in the spectrum at 2θ values of 11.6° and 12.8° (with an uncertainty of ±0.2°), representing crystalline d-spacing of 7.62 Å and 6.91 Å respectively. As the film thickness increases, the diffraction signal increases due to the growth of the materials incorporated in the diffraction process. Meanwhile, the full width at half maximum (FWHM) bandwidth decreases with the increase of the film thickness. According to the Scherrer formula [19], the decrement reflects the decrease in the internal microstrain within the films and an increase in the crystallite size. However, the increased crystallite size makes the film surface rough, as shown in Fig. 2. From Fig. 2 and Table 1, we reach a conclusion that surface roughness increases with the increase of the thickness, which leads to the increment of scattering loss, thus reducing the fluorescence efficiency of the Lumogen coating.

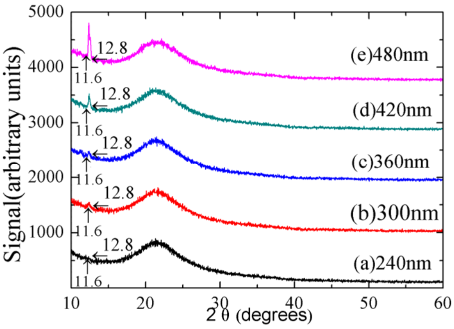


FIG. 1. XRD patterns of Lumogen thin films with the different thicknesses of (a) 240 nm, (b) 300 nm, (c) 360 nm, (d) 420 nm, and (e) 480 nm.

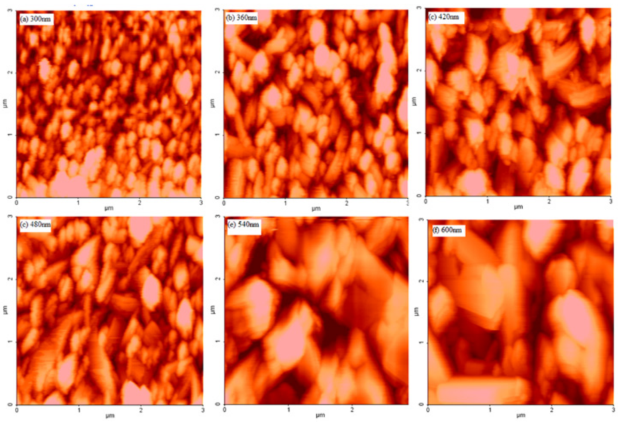


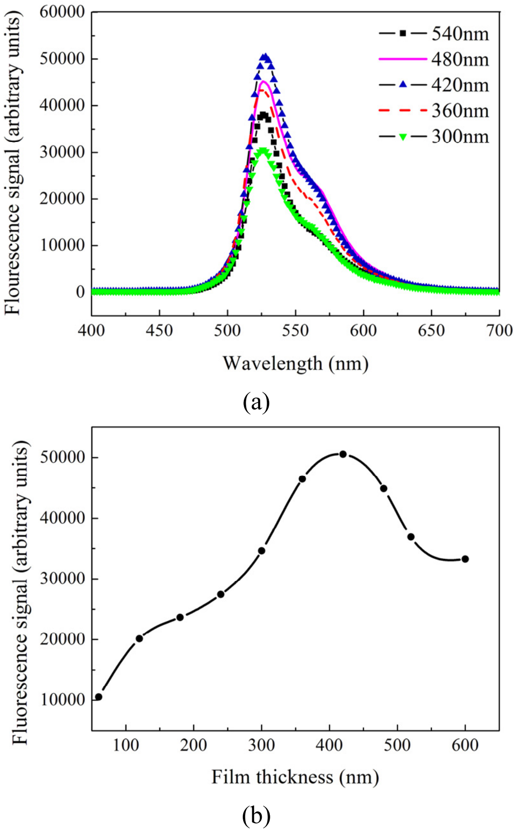
FIG. 2. AFM micrograms of the films with thicknesses of (a) 300 nm, (b) 360 nm, (c) 420 nm, (d) 480 nm, (e) 540 nm, and (f) 600 nm.

Photoluminescence (PL) spectra here refer to the action of fluorescence related signal variation at a fixed wavelength of excitation light. Figure 3(a) shows the emission spectrum of samples with different film thicknesses excited at 250 nm. The peaks of fluorescence spectrum occur at about 528 nm, which is in the sensitivity region for most CCD/CMOS.

As shown in Fig. 3(b), the light emission is changing with the increase of the film thickness. Meanwhile, an inflection point of PL signal occurred at about the thickness of 420 nm. It is known that visible luminescence is mainly due to the azomethine structure and a lot of double bonds

TABLE 1. AFM test data of Lumogen films with different thicknesses

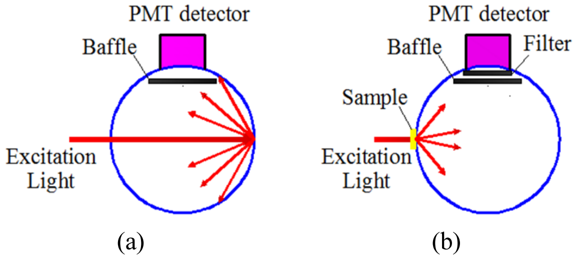
Film thickness (nm)	300	360	420	480	540	600
Rq (nm)	22.443	27.949	28.745	43.496	47.549	79.649
Ra (nm)	17.136	21.863	21.027	33.807	37.960	64.509



(a)

(b)

FIG. 3. (a) photoluminescence spectrum of samples, where the excitation wavelength is 250 nm and the thicknesses of Lumogen films are 300 nm, 360 nm, 420 nm, 480 nm, 540 nm (b) Fluorescence peak signal of samples with different thicknesses of Lumogen.



(a) (b)

FIG. 4. Diagram illustrating the two configurations of the sphere required for the CE measurement. (a) Measurement of excited energy, (b) Measurement of emitted energy.

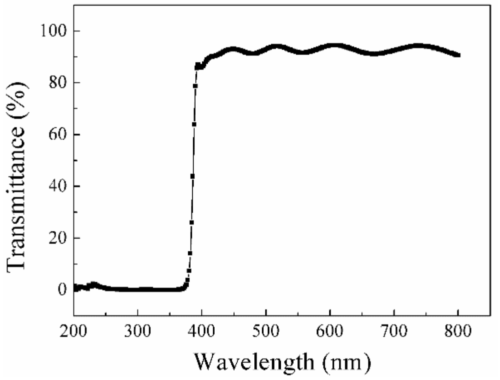


FIG. 5. Transmittance of the filter with cut off wavelength of 399 nm, whose function is to filter the ultraviolet excitation light.

of Lumogen molecules [20]. The emission signal is abruptly enhanced and slightly affected by low surface roughness, when the thickness is less than about 420 nm. With the increase of the thickness, the inner coating close to the substrate shows weaker fluorescent radiation because of limited UV penetration depth. On the other hand, the enhanced surface roughness increases the scattering loss of incident UV light and thus reduces the conversion efficiency. Thus the ultraviolet sensitivity cannot be improved by only increasing the film thickness infinitely.

Conversion efficiency (CE) of phosphor coatings is the ratio of emitted light photon in the visible and exciting light photon in the ultraviolet. The integrating sphere is used in the spectrophotometer for the measurement of emitted light (visible) and incident light (ultraviolet). According to the definition of CE, the excitation photon number n_{inc} after incident to the luminescence film and the emission photon number n_{emi} emitted by the luminescence film after excitation, are measured. The CE of the Lumogen film is obtained if the property of emission spectrum of the different excitation wavelengths is considered.

As shown in Fig. 4, the excitation light of wavelength λ_{inc} is incident on the integrating sphere and is measured by the detector. The excitation photons n_{inc} can be obtained by

$$n_{inc} = \frac{E_{inc} \times \lambda_{inc}}{hc} \tag{1}$$

where h is Planck's constant, c is the speed of light, and E_{inc} is the energy of the excitation light.

The excitation light through the film should be eliminated once the radiation photons are measured. Thus a long wave pass filter (LPF) is placed at the front of the detector to filter the excitation light. After the excitation light irradiates the film sample, the light emitted from the sample is transmitted to the integrating sphere through the base glass, and then the energy E_{emi} is detected by the detector after filtering out the interference light. The transmittance of the LPF is shown in Fig. 5. Considering the transmittance varying with the wavelength, the energy of emission wavelength through the filter can be expressed as

$$E_{emi} = \sum_{m}^{n} E(\lambda_i) T(\lambda_i) \tag{2}$$

where the $E(\lambda_i)$ and $T(\lambda_i)$ are the energy and the transmittance of the emission wavelength, respectively.

The transmittance of the filter is different for different wavelengths, so it is necessary to calculate the emission energy of different wavelengths by means of the emission spectrum of the luminescent film and the transmittance spectrum of the filter. The emission photon number of the corresponding wavelength is calculated, and then the total emission photon number is obtained.

Emission spectra of luminescent thin films were obtained by a fluorescence spectrometer and the scaling factor $k(\lambda)$ of the total energy of each sampling wavelength is given by the discrete method. The range of the emission wavelength is from λ_m to λ_n, and $E(\lambda_i)$ is the energy of the emission at wavelength λ_i. Considering the transmittance of the emission wavelength, the ratio of energy of the wavelength to the total energy is obtained by

$$k_T(\lambda_i)=\frac{E(\lambda_i)T(\lambda_i)}{\sum_m^n\left(E(\lambda_i)T(\lambda_i)\right)} \tag{3}$$

Here, the $k(\lambda_i)$ value is equal to the $k_T(\lambda_i)$ value. The energy of the emission wavelength λ_i can be obtained based on

$$E(\lambda_i)=\frac{k_T(\lambda_i)E_{emi}}{T(\lambda_i)} \tag{4}$$

Thus, the number of radiation photons is

$$n_{emi}=\sum_m^n\frac{E(\lambda_i)\times\lambda_i}{hc} \tag{5}$$

Then the conversion efficiency of the excitation wavelength λ_{inc} is

$$\eta_{CE}=\frac{n_{emi}}{n_{inc}}=\sum_m^n\frac{k_T(\lambda_i)\times E_{emi}\times\lambda_i}{T(\lambda_i)\times E_{inc}\times\lambda_{inc}} \tag{6}$$

Figure 6 is the CE variation of the samples with different thicknesses of Lumogen film. Obviously, there is an optimal thickness of 420 nm at the four exciting wavelengths. The dependence of CE on the thickness of phosphor coatings is in good agreement with the PL spectrum and wavelength. Moreover, the CE is higher at shorter exciting wavelength than at longer exciting wavelength, which is favorable for fabrication of high sensitive UV-responsive CCD.

Quantum efficiency is a fundamental property of CCD to indicate the amount of current that the CCD will produce when irradiated by photons of a particular wavelength. It is defined as the ratio of accumulated electrons to radiated photons of a single pixel, when the CCD chip is irradiated at a specific wavelength for a certain exposure time [21].

A schematic of the measurement of QE is presented in Fig. 7. A collimated and uniform beam of light from a xenon lamp illuminates the CCD or CMOS. Before the measurement, the signal of the light is calibrated by a photo-radiometer. The computation of the QE requires the measurement of the mean gray values and the temporal variance of the gray together with the irradiance per pixel in the unit photons or pixels, is called the photon transfer method [21].

A series of CCDs coated with different film thicknesses were fabricated. As shown in Fig. 8, it is found that the

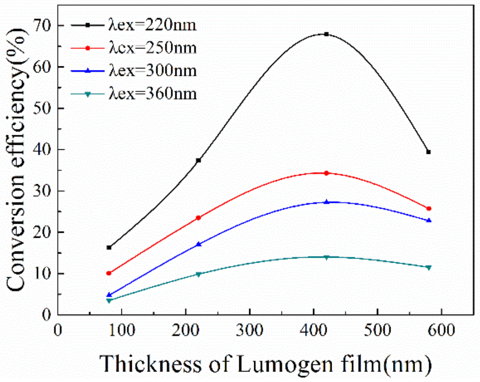


FIG. 6. The conversion efficiency of four samples with different thicknesses of Lumogen film (80 nm, 220 nm, 420 nm, and 580 nm) excited at wavelengths (220 nm, 250 nm, 300 nm, and 360 nm).

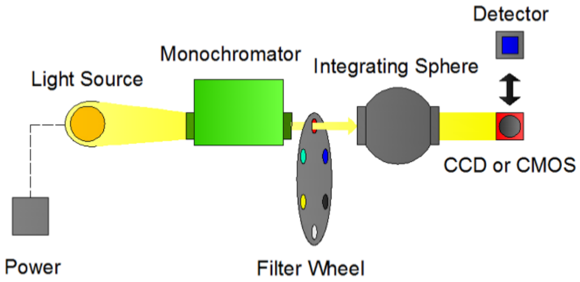


FIG. 7. Schematic diagram of measuring system of QE.

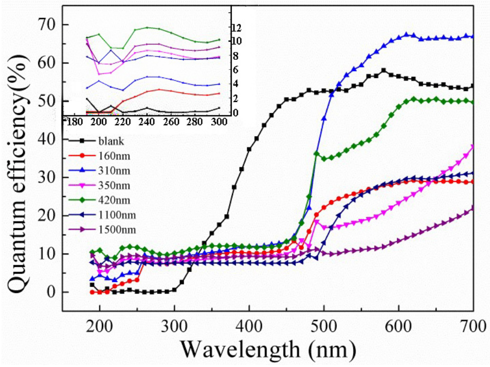


FIG. 8. The quantum efficiency of CCDs with different thickness of Lumogen films (blank, 160 nm, 310 nm, 350 nm, 420 nm, 1100 nm, 1500 nm). The detailed figure of QE in the range of 190 nm to 300 nm is on the top left corner.

QE enhancement of the coated CCDs changes with different thicknesses in the UV wavelength. Meanwhile, there is not significant decrease in visible response and resolution by the presence of Lumogen. It is obvious that the coated CCD has the maximum QE when the thickness of the Lumogen film is about 420 nm. This is in agreement with the outcome of the measurement of CE. The QE in UV is typically 8% to 12%, while uncoated CCD is 0% at the range of 200 to 310 nm.

IV. CONCLUSION

The PL signal and CE of the phosphor coating strongly depend on the film thickness. The depth of the ultraviolet absorption and surface scattering of the phosphor coating are considered as essential factors. According to the XRD and AFM results, the surface roughness of Lumogen film increases with the increase of thickness. The Lumogen phosphor coating with the thickness of around 420 nm has the largest luminescent signal and conversion efficiency in the UV spectrum. Besides, CCDs coated with Lumogen film of the same thickness had the maximum quantum efficiency in the range of 190~340 nm. These results provided one key processing parameter for improving the sensitivity of Lumogen coated CCDs to ultraviolet light.

ACKNOWLEDGMENT

This work was partially supported by the National Science Instrument Important Project (2011YQ14014704), Shanghai Municipal Science Instrument Important Project (14142200902), National Natural Science Foundation of China (61378060, 61205156), Shanghai Science and Technology Innovation Action Plan (17142202700).

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