STABILITY OF LUMOGEN FILMS ON CCDs

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ABSTRACT

Fluorescent lumogen films are now widely used for improving the UV quantum efficiency of CCDs and other silicon photodetectors. Because of the organic nature of lumogen and its low melting and boiling points, stability of the films has been in question. We present results of stability tests in which quantum efficiency and film characteristics are evaluated with respect to exposure to illumination, elevated temperature, and reduced pressure. Our results indicate a high tolerance to UV and visible illumination, and to slightly elevated temperatures (95°C) at normal operating pressures. However, high vacuum conditions (10^{-6} torr) can produce voids in the films at even slightly elevated temperatures.

Keywords: lumogen, fluorescent coatings, UV detectors, charge-coupled device

1. INTRODUCTION

Lumogen films have proven to be a highly efficient and simple method for improving the UV response of CCDs and other silicon photodetectors. 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[1]) are a result of its organic nature. It is, however, the organic nature of lumogen which brings into question its stability.

2. PHYSICAL AND CHEMICAL PROPERTIES

Lumogen decomposes at its melting point--about 295°C.[2,3] With a strong tendency to form into elongated crystals when evaporated or melted, lumogen has been evaporation deposited at temperatures as low as 150°C, indicating a significant vapor pressure at this temperature.[3,4] Lumogen's chemical structure contains four phenyl rings, as shown in Fig. 1, which are often associated with luminescence in organic materials.[5] Interestingly, molecules with ring structures (aromatic hydrocarbons) are more stable against UV radiation than are linear chain-type (aliphatic) molecules.[6]

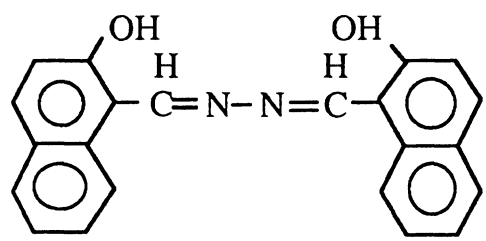

Fig. 1. Lumogen structure

0-8194-1762-9/95/$6.00

3. CONVERSION EFFICIENCY

The conversion efficiency of lumogen films can be estimated by evaluating their performance on CCDs. The peak emission of lumogen is at 525nm. 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.

4. VACUUM STABILITY

To test the stability of films in closed system vacuum, lumogen coated glass plates were vacuum sealed in pyrex tubes for extended periods of time. Prior to sealing, the samples were continuously pumped for 72 hours at 2×10^{-6} torr to degas the tubes. Samples held under vacuum for 38 and 122 days at room temperature showed an increase in crystallite size when compared with samples kept in air for the same period of time. Increased crystallite size in itself does not appear to greatly affect QE, as described in the next section, as long as the coating is not lost through evaporation.

The evaporation rate of a lumogen film under continuous evacuation was determined by measuring deposition rates onto a Maxtek quartz crystal thickness monitor from a heated source in a vacuum chamber. A thick film, produced by mixing lumogen with toluene, was spread onto the surface of an aluminum block fitted with a heater. The thick film was necessary to avoid complete evaporation during the measurement. The experiment was carried out at a pressure of approximately 10^{-6} torr (Fig. 2).

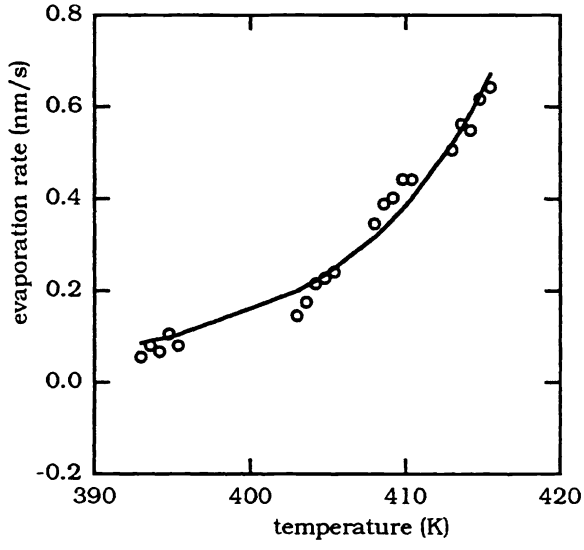

Fig. 2. Lumogen evaporation rate at 10^{-6} torr. Solid line: $\log(\text{rate}) = -113.3557 + 17{,}126/T + 0.13871T + 5.4728\log T$.

5. THERMAL STABILITY

Two experiments were performed to determine the thermal stability of lumogen films. In the first experiment, lumogen coated glass slides were sealed into two pyrex tubes--one sealed at atmospheric pressure, the other at $2x10^{-6}$ torr. The tubes were submerged in a water bath heated to 95°C and held there for 15 hrs. Photomicrographs of the films are shown in Fig. 3.

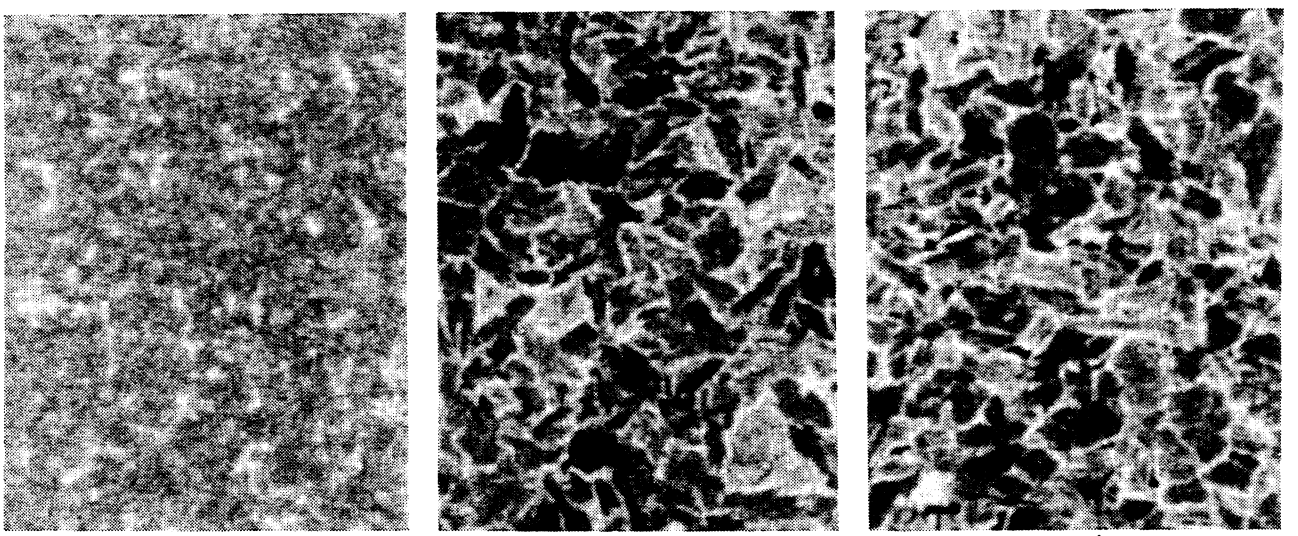

Fig. 3. Lumogen films heated to 95°C for 15 hrs. Left to right: as-coated, air-sealed, vacuum-sealed. Voids can be seen in the vacuum sealed sample. Mag. 1200x.

Compared with a control sample which was not heated, the crystallite size in the heated films was considerably larger. A striking difference between the two heated samples is that the sample sealed in vacuum had developed voids between crystallites as shown in the figure, while no such voids could be found in the sample sealed at atmospheric pressure (or samples sealed in vacuum for up to 122 days, see above). Since both heated samples were maintained in a closed environment, there should be no driving force for evaporation once the vapor pressure of lumogen is established in the tubes. However, there is a driving force for crystallite growth to reduce interfacial area.[7] Because of the impediment from the air molecules in the air-sealed tube, crystallite growth in this sample must have occurred primarily by diffusion. However, in the sample heated in vacuum, crystallite growth through vapor transport would not be impeded. Thus voids could form as a result of transport of material from smaller, higher surface energy crystallites, to larger ones.

A second thermal experiment was performed to determine the effect of heating and consequent change in crystallite size in the films on quantum efficiency. A hot air gun was directed at the surface of a freshly coated CCD. Most of the CCD was shielded with a metal plate, leaving one edge exposed to the direct blast of hot air. The heat was removed when a change in the appearance of the exposed part of the film was noticed. An image from the CCD produced with 400nm filtered incandescent light (flat field corrected using 700nm filter in the same optical test fixture) indicated that the QE had been reduced in the heat exposed area. The CCD temperature required to bring about this change is unknown, however a thermocouple placed under the CCD package read a maximum

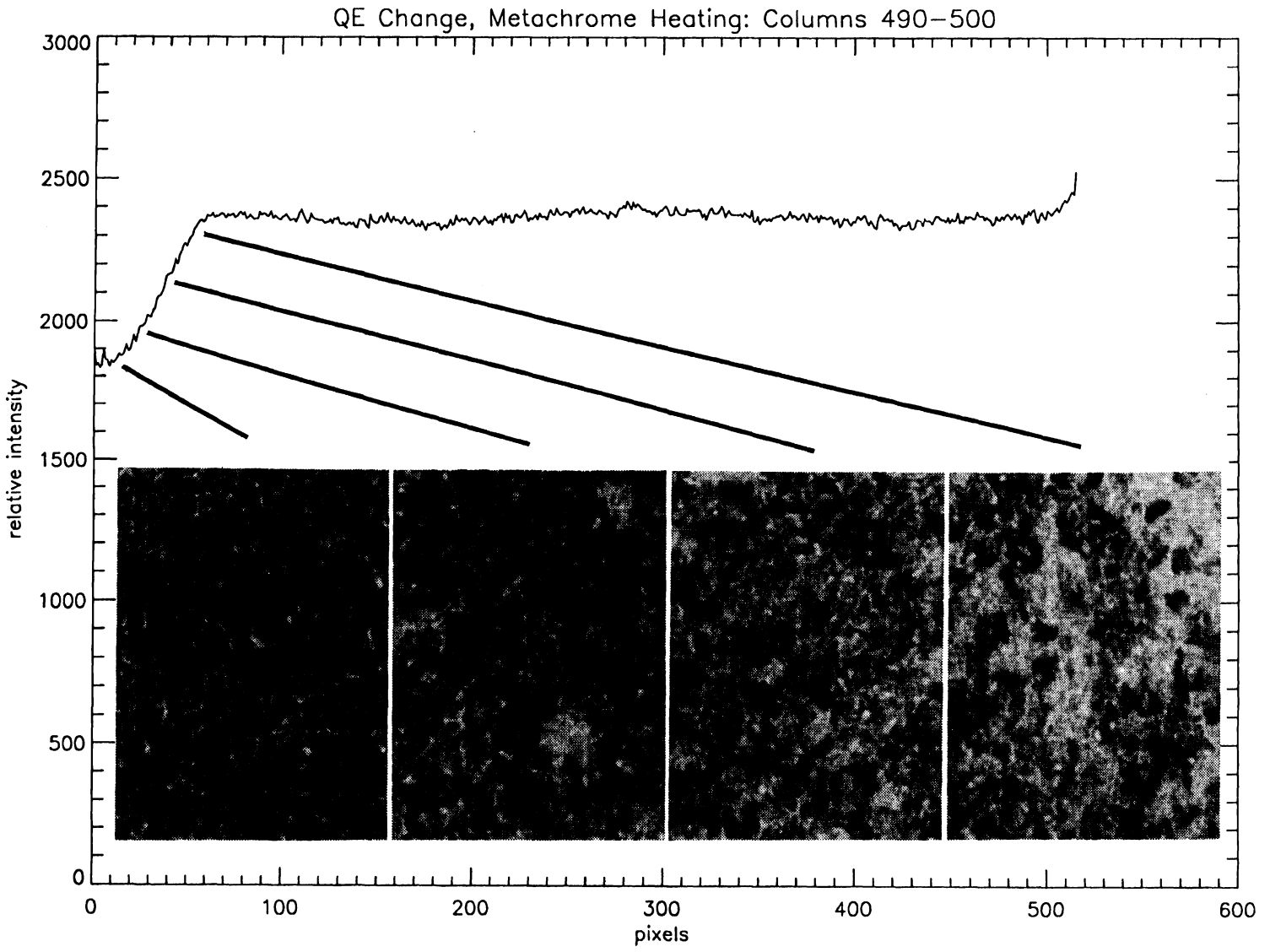

Fig. 4. Intensity plot for 10 columns (averaged) of the heated, lumogen-coated CCD and corresponding photomicrographs. Mag. 900x.

package temperature of approximately 100°C while the CCD surface temperature was in excess of this.

A plot of intensity versus distance from the edge of the CCD as well as photomicrographs of the heated area are shown in Fig. 4. The heat produced voids in the films, similar to the results of Fig. 3. The reduction of QE in the heated portion of the film is roughly proportional to the void fraction. Thus, it appears that voids in the films, rather than grain growth, is the primary reason for the lower QE.

6. UV STABILITY

6.1. Narrow Band

The experiment consisted of exposing lumogen coated and uncoated portions of a CCD to intense (1.4×10^{14} photons/cm^2/s) 253nm light of narrow bandwidth for an extended period of time. By dividing the CCD into quadrants with the following conditions: 1) coated and exposed, 2) coated and unexposed, 3) uncoated and exposed, and 4) uncoated and unexposed, precise measurement (+/- 0.1% change in QE) could be made of the effects of the UV radiation. Figure 5 shows the quantum efficiency of each quadrant of the CCD for an exposure time of 15 hours. The change in quantum efficiency caused by the UV exposure is given in Fig. 6. The results show that the CCD itself is affected by UV and that the change in QE of the lumogen coated portion is similar to the effect in the uncoated CCD. Thus we can detect no measurable degradation in the coating from the UV exposure. The intensity of the UV light used in the experiments is sufficient to saturate a CCD pixel in a few thousandths of a second.

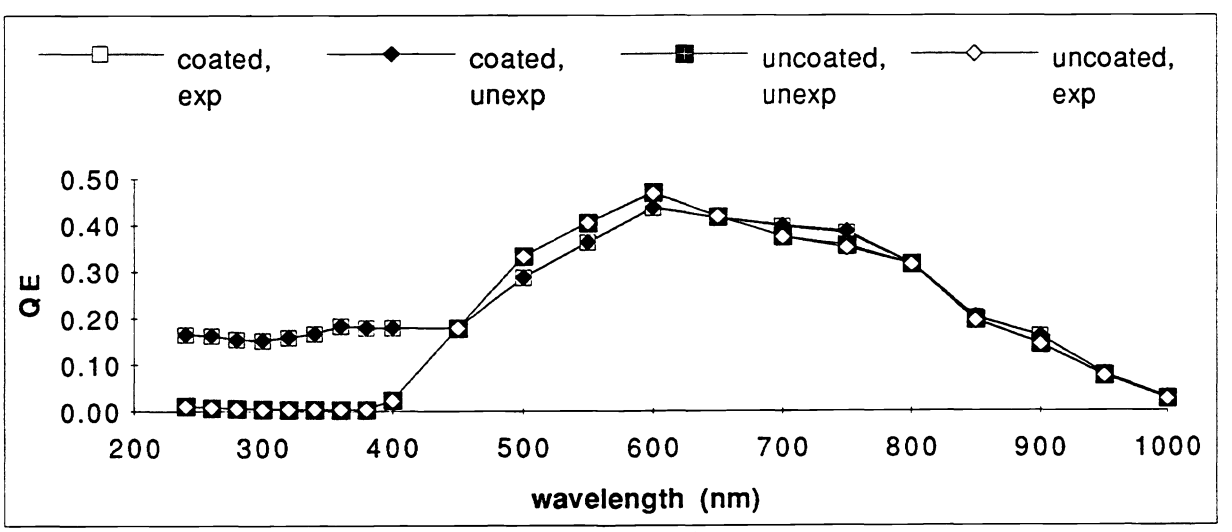

Fig. 5. QE of the test CCD for the four conditions.

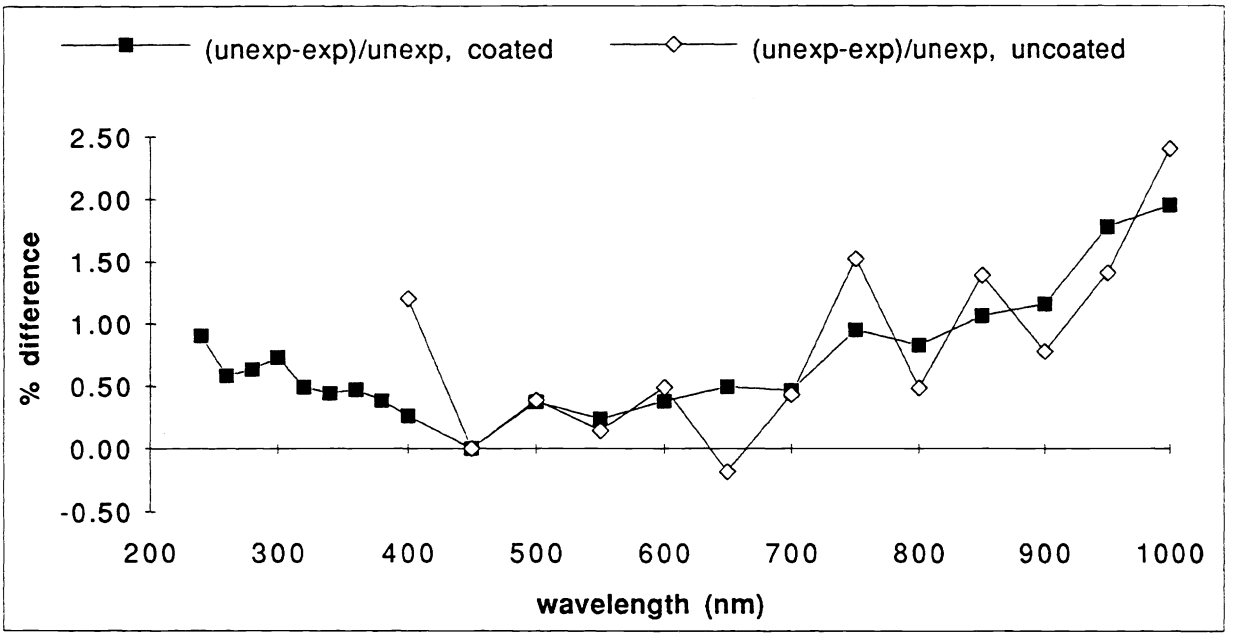

Fig. 6. Differences in QE between exposed and unexposed halves of the test CCD.

6.2. Broad Band

To test the stability of lumogen films to broad band UV, a coated CCD (within an evacuated camera head) was exposed to unfiltered light from a mercury pen lamp. The lamp was located approximately 2cm from the CCD to produce an extremely high exposure. A cover plate with a small hole to localize the exposure on the CCD was placed over the CCD. The intensity of exposure was estimated by measuring the exposure time needed to saturate the CCD with the lamp further away (to allow for reasonable shutter times), correcting for the distance, and assuming a flat 12% QE for the device in the UV. An estimate of 6×10^{15} photons/cm^2/s for the original exposure condition was obtained. A 30 minute exposure at this level produced less than 1% change in QE in the exposed area in a 400nm image. A 14.5 hour exposure produced similar results. After venting the camera to air, the CCD was again exposed at the same intensity. Exposure times of 40 minutes and 15 hours again produced <1% change in QE.

7. CONCLUSIONS

Lumogen films are highly efficient as UV converters for CCDs and other silicon photodetectors. Although the 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.

REFERENCES

1. McGraw-Hill Encyclopedia of Physics, S.P. Parker ed., p. 354, McGraw-Hill Book Company, New York, 1983.
2. BASF Material Safety Data Sheet, BASF Corporation, Chemicals Division, 491 Columbia Avenue, Holland, MI 49423.
3. N. Kristianpoller and D. Dutton, "Optical Properties of "Liumogen": A Phosphor for Wavelength Conversion", Applied Optics, Vol. 3, No. 2, pp. 287-90, Feb. 1964.
4. W.Viehmann, C.L. Butner, and M.W. Cowens, "Ultraviolet (UV) sensitive phosphors for silicon imaging detectors", Ultraviolet and Vacuum Ultraviolet Systems, SPIE Vol. 279, pp. 146-52, 1981.
5. H.W. Leverenz, An Introduction to Luminescence of Solids, Dover Publications, New York, 1968, p. 250.
6. Z. Jastrzebski, The Nature and Properties of Engineering Materials, p. 473, John Wiley and Sons, New York, 1976.
7. A. Guy and J. Hren, Elements of Physical Metallurgy, p. 448, Addison-Wesley, Reading, Massachusetts, 1974.