Soft-x-ray damage to *p*-terphenyl coatings for detectors

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The organic phosphor *p*-terphenyl is used as a wavelength-converter coating in some soft-x-ray detectors. We have measured the absolute photoluminescent efficiency of *p*-terphenyl as a function of incident photon energy from 36 to 191 eV. We have also measured changes in the efficiency caused by soft-x-ray fluence (total photons absorbed per unit area) at several photon energies in this range. We find that efficiency drops rapidly as a function of fluence, with the rate of decrease increasing with higher soft x-ray energies.

Key words: *p*-terphenyl, phosphor, photoluminescence, soft x ray, detector, efficiency, photon damage.

Phosphors are a practical and relatively inexpensive method for converting soft x rays to visible light. Because devices such as photodiodes, photodiode arrays, photomultipliers, and charge coupled devices are optimized for detecting visible and ultraviolet light, phosphors coupled to these devices make excellent soft-x-ray detectors for some applications.[1–3]

The organic phosphor *p*-terphenyl has been used as a coating for photomultiplier tubes used in detection of visible, ultraviolet, and vacuum-ultraviolet Cerenkov radiation.[4] It has also been mentioned several times as a choice for a conversion material in the soft-x-ray region.[5–7] Because uniformity is particularly important for multichannel devices, an advantage of organic phosphors is that it is relatively simple to make an even film by evaporation or spray application.[1,7]

To the best of our knowledge, an issue that has not been addressed by those who have studied *p*-terphenyl coatings as recently as 1991[5–7] is the question of whether the conversion efficiency is degraded by soft x rays. Because we now have soft-x-ray sources capable of delivering photon fluxes many orders of magnitude greater than those available when organic phosphors came into use as detectors, this is a question of increasing importance. We previously measured the light output of sodium salicylate, a popular organic phosphor, and we found that it is noticeably reduced under exposure to soft x rays of 30–153 eV.[8,9] Similar changes in its efficiency at energies below 15 eV had previously been noted.[10,11] Because *p*-terphenyl had been suggested as a substitute, we have now tested it for photon damage also.

Our raw material was Aldrich[12] 99+% purity *p*-terphenyl. Evaporation is the technique favored by other authors[5–7]; it does not require that the substrate be heated and is therefore a good method for directly coating devices with a thin, uniform layer. The technique has its drawbacks; the evaporation system must be thoroughly cleaned afterward, and the *p*-terphenyl layer obtained is cloudy and thus scatters the emitted light. Because most of the light is created close to the front surface, for a thick scattering film only a small percentage of the emitted light will exit from the back surface.[13] A film produced by melting powder on a glass cover slip and allowing it to cool slowly is much clearer and can be quite thick. The resulting film is cracked and polycrystalline; loose surface flakes can be removed with a razor blade. Under irradiation both kinds of sample behaved similarly. The damage data presented here are from samples melted onto substrates, because their thickness guarantees that all the incident photons are absorbed in the sample.

The data were taken at beam line 8 of the Synchrotron Ultraviolet Radiation Facility storage ring at the National Institute of Standards and Technology. Multiple-order soft x rays were removed through the use of elemental filters. The samples were mounted in aluminum sample holders; care was taken not to expose the samples to the beam until data taking commenced. The emitted light was detected by

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United Detector Technologies PIN-6DP silicon photodiodes[12] located behind the glass cover slips. The photodiodes were run in an unbiased mode, and the photocurrent was detected by a Keithley 617 electrometer.[12] Incident photon flux was determined by using a United Detector Technologies X-UV-100 calibrated silicon photodiode.[12,14–16] Because of experimental constraints, the samples were oriented 55° from normal to the beam. All measurements were taken at room temperature.

For damage studies we measured the change in the efficiency, defined as the number of visible light photons produced per soft-x-ray photon absorbed, as a function of fluence. The fluence is defined as the total number of photons absorbed per unit area. Shown in Fig. 1 are measurements at 67.1, 88.7, and 155 eV, with the initial value normalized to 1.0. With a flux in the 10^{11} photons/cm^2 s range, each of these runs represents less than 2 h of exposure; data points were taken at 12-s intervals. The damage rate increases with incident soft-x-ray energy. We also tried turning off the soft-x-ray beam for several minutes, but we saw no evidence that the efficiency recovered. Samples showed no visible evidence of color change after being exposed. Uncertainties, quoted as σ values, include systematic contributions to the fluence from the calibration of the soft-x-ray photodiode, 12%,[14] and an estimate of the beam spot size, 20%, leading to a root-sum-square error of 23%. The normalized efficiency includes a random uncertainty of 5% as a result of fluctuations in the visible-light measurement.

In our previous research on sodium salicylate, we found that the energy threshold for photon damage occurred at approximately twice the band gap of the material.[8,9] If *p*-terphenyl behaves in a similar manner, its damage threshold is approximately 10 eV. We hope to publish additional research on this subject at a later time.

We also measured the efficiency versus photon energy of an evaporated *p*-terphenyl sample from 36 to 191 eV, as shown in Fig. 2. Data were measured from high energy to low energy on a sample that had been exposed for 30 min at 38 eV. The scatter below 55 eV is due to a low signal. Because the sample was damaging as a function of both time and energy, the data points at the lower energy probably have slightly higher values relative to those at higher energies than our data show. We found that the efficiency was rising fairly linearly with energy. In addition, we based the absolute value of the efficiency on the initial light output of the damage runs. This efficiency represents the total number of photons emitted by the *p*-terphenyl per extreme ultraviolet photon absorbed; in actual use, a diode behind an evaporated *p*-terphenyl converter film will detect fewer photons, both because of the limited angle of detection and because of light scattering in the film.[13] We estimate systematic contributions to uncertainty in the absolute efficiency measurements as follows: correction for scattering within the sample, estimated by visible-light measurements, contributes 17%; estimate of the collection solid angle of the visible-light diode, 3%; sensitivity of the diode over the emission spectrum of *p*-terphenyl,[6] 5%; measurement of the incident flux, 12%; and extrapolation to zero exposure of the sample, 5%. Coupled with the 5% random uncertainty in the light output reading, this leads to a root-sum-square uncertainty of 23%.

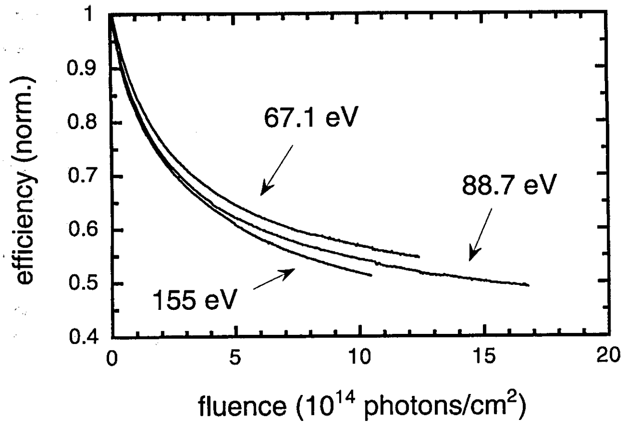

Fig. 1. Efficiency as a function of soft x-ray fluence at three different incident photon energies. The initial value was normalized to 1.0.

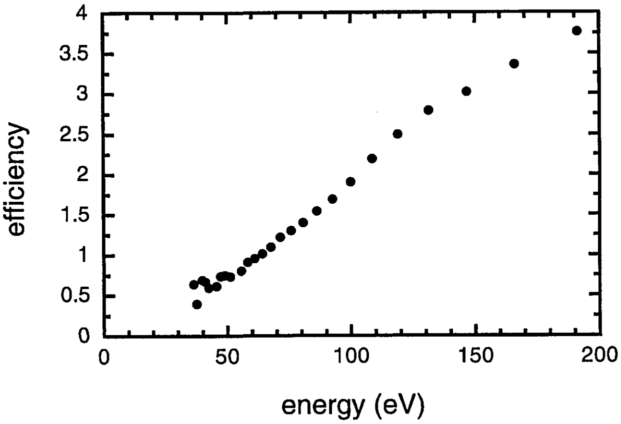

Fig. 2. Absolute efficiency as a function of incident photon energy.

It would seem that historically there has been a common belief that the efficiency of organic phosphors is a constant in the vacuum ultraviolet. This is probably due to the early measurements of the efficiency of sodium salicylate, which were then extrapolated further in energy for its use as a constant reference standard.[1,17] The *p*-terphenyl measurements of Dyjak *et al.*[5] go from 40 to 99 eV and are interpreted with the assumption that efficiency could not be rising as incident photon energy rises. The data of Stutman *et al.*[7] are also interpeted as indicating a relatively flat efficiency in the energy range 1.5–5 keV; it is possible that soft x-ray damage and the thinness of their phoshor layers affected their results.

Efficiency rising with incident photon energy is consistent with the behavior of other phosphors.

Phosphor efficiencies have a great deal of structure as a result of the surface recombination of charge carriers at energies at which their absorption coefficients are rapidly changing, but otherwise efficiencies rise approximately proportional to the energy.[18–20] Although the efficiency curve in Fig. 2 is rising fairly linearly, if these data were carried to lower energies the slope would decrease, as with most phosphors, because the absorption coefficient of p-terphenyl has a broad peak at 20 eV (Ref. 21), creating shape in the efficiency as a result of surface-recombination effects.[18,19]

In detector use, the conversion efficiency will eventually drop off as one goes to higher energy x rays with lower absorption coefficients, as some photons will penetrate through the phosphor layer. However, one must then be concerned with the possibility of x-ray damage to the visible-light diode behind the phosphor.

Because both sodium salicylate and p-terphenyl, two of the most commonly used organic phosphors, are damaged by soft-x-ray photons, we believe it is prudent to consider all organic phosphors to be potentially susceptible to this kind of damage.[22] In our experience, certain oxide phosphors are quite stable as a function of soft x-ray fluence and are as efficient or more efficient than organics as converters of soft x rays to visible light.[18–20] In addition, for single-channel detectors, soft-x-ray optimized diodes are highly efficient, convenient, and generally quite linear in efficiency.[7,14–16] Whenever possible, we recommend using either of these alternatives to p-terphenyl and other organic phosphors in detectors for soft x rays.

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