Fabrication of Gd$_2$O$_2$S:Tb based phosphor films coupled with photodetectors for x-ray imaging applications

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The Gd$_2$O$_2$S:Tb based phosphor coupled with photodetectors has been widely used in digital x-ray imaging applications. The key issues associated with phosphor film are x-ray absorption and conversion efficiency, spatial resolution, deposition uniformity, and integration with the imaging array. In this article we report on experimental studies of the phosphor film synthesis, deposition, and characterization. A composite material, consisting of Gd$_2$O$_2$S:Tb, polyvinyl alcohol, and water coupled with a small amount of additives, is synthesized as a phosphor paste. The parameters controlling film quality include individual component concentrations, grain sizes of phosphor, and viscosity of the solution. A sedimentation technique is used to deposit the phosphor directly on the imaging array. A number of phosphor films have been synthesized with the particle sizes ranging from 2.5 to 25 μm and film thickness ranging from 85 to 1100 μm, and measurement results of x-ray conversion efficiency and spatial resolution in terms of modulation transfer function are presented. A new technology for phosphor patterning is proposed to seamlessly integrate the phosphor with the photodetectors by using negative photoresist SU-8 and preliminary results are presented. © 2002 American Vacuum Society.

I. INTRODUCTION

Digital x-ray imaging is a rapidly developing technology for radiography applications, including airport security inspection and medical diagnoses. There are two typical x-ray detection schemes: one is direct detection and the other is indirect detection. The former comprises a thick amorphous silicon or heavy metal Schottky diodes to directly sense the x-rays. The latter consists of an array of thin film a-Si:H optical detectors with an overlaying phosphor film. The phosphor film serves to convert incident x-rays into visible radiation which is then sensed by the a-Si:H detector array. Two major phosphors, CsI:Tl and Gd$_2$O$_2$S:Tb, are widely used in indirect x-ray imaging applications. The uniformity of the phosphor film over a large area is essential for a high quality image. Therefore the deposition technique should be able to provide this large area uniformity for the desired film thicknesses and powder sizes. A sedimentation technique is adapted for film deposition in our work. By adjusting the chemical composition of paste materials and operating parameters of sedimentation, a series of the phosphor films with Gd$_2$O$_2$S:Tb particle sizes from 2.5 to 25 μm and film thicknesses from 85 to 1100 μm have been fabricated. As an x-ray converter, the phosphor film must be thick enough to enable a significant fraction of the incident x-rays to interact and produce sufficient optical photons for detection. The optical photons generated inside the phosphor while traveling to the detectors will be reflected by phosphor particles to produce crosstalk within adjacent detectors consequently degrading image quality. The thicker the film, the higher is the reflection of optical photons inside the film. There is a trade-off between the phosphor film thickness and image quality. The practical film thickness should be determined by the specific applications. For example, in the medical applications, the phosphor films used for mammography are thinner than those for radiography due to the high spatial resolution requirement of mammography. The requirement to increase the spatial resolution without reducing the light signals becomes more crucial in many applications. Patterning the phosphor film that leaves phosphor material only on top of the detectors can significantly reduce the cross talks. Because the thickness of the phosphor layer is over several hundred microns and the size of the photodiode is less than 200 μm, traditional methods for patterning the phosphor are impractical. An epoxy based negative photoresist SU-8 has been widely used in MEMS to provide thick and high aspect ratio patterns. Here we are using SU-8 to form patterned “tubs” on top of the detector areas where the phosphor material can be directly deposited or filled. The SU-8 can be patterned by standard UV lithography and the thickness of the SU-8 layer can be several hundred microns.

II. FABRICATION OF PHOSPHOR FILMS

The coating solution consists of three major components: Gd$_2$O$_2$S:Tb, polyvinyl alcohol (PVA), and H$_2$O coupled with a few organic additives. The composite material provides several controllable parameters including concentrations of individual chemicals, particle size of the phosphor, and viscosity of the solution. The coating solution was first prepared by dissolving 3–10 wt % PVA into deionized water at 85–95 °C with proper agitation to avoid dead zones where PVA could agglomerate. After the PVA was fully dissolved, the...
solution was naturally cooled down to room temperature and poured into a vertical cylindrical, flat-bottomed glass vessel for mixing with phosphor particles. The solution in the vessel was stirred, then a small amount of the additives was introduced followed by gradual addition of weighted phosphor particles. The overall mixing process must be subject to agitation until the phosphor particles were able to fully disperse into the polymer matrix. Here, the rate of agitation played a critical role. It must yield enough centrifugal force to keep the phosphor particles suspended in solution for dispersion. Meanwhile overagitation should be avoided since it can generate a large volume of foams that may remain and entrain into the film later. A Calramo BDC 6015R stirrer with a digitally controlled brushless dc motor was used for agitation control. A three-bladed impeller was mounted on the shaft near the bottom of the vessel. By a series of preexperiments, the agitation rates were carefully determined as functions of the phosphor particle sizes and PVA concentrations in the range from 600 to 1300 rpm. Agitation was terminated when the particles were fully dispersed and then a homogeneous coating system was achieved. The solution was then immediately but slowly transferred into a settling cylinder. The cylinder has a high aspect ratio (wall/diameter = 8/1) and a transparent wall to visually monitor the phase separation. Figure 1 shows the phase separation after 6 h of sedimentation. During the sedimentation process, the phosphor particles are separated by gravity. On top of the solution is the transparent polymer solvent where phosphor particles have been fully separated from the solution, while at the bottom is a homogeneous phosphor solution. Between these two phases, a phase separation interface is formed where the sedimentation process is taking place. The sedimentation velocity is directly proportional to the weights of the phosphor particles that are related to particle sizes and inversely proportional to solution viscosity. When all of the particles settled down completely, the phosphor-coated substrate was removed and cured in a fume hood with controlled humidity and temperature. The phosphor grain size and distribution have a significant impact on the final phosphor film after sedimentation. Figure 2 shows the vertical distribution of phosphor particles with different grain sizes. At the same loading density, the film with smaller particles [Fig. 2(a)] is much thinner and compacter than that with larger particles [Fig. 2(b)].

### III. CHARACTERIZATION OF PHOSPHOR FILMS

#### A. X-ray conversion measurements

X-ray conversion efficiency is an important property of the phosphor film for imaging applications. For an energy, $E_{in}$, of incident x-rays, the conversion efficiency $\eta$ can be expressed as:

$$\eta = \frac{N_{\text{light}}E_{\text{light}}}{E_{in}}.$$  

Here, $N_{\text{light}}$ is the total number of optical photons emitted upon interaction with an x-ray quantum and $E_{\text{light}}$ is the associated mean energy of emitted photons. This conversion efficiency is also called the energy conversion efficiency. The emission spectra of light from Gd$_2$O$_2$S:Tb phosphor is a discrete distribution between 500 and 900 nm and has a peak at 560 nm (green light). The incident x-ray energy was calculated by integrating the x-ray spectrum under a certain source voltage, which was determined through a computer simulation program under specified settings of a medical x-ray machine. The green light energy was measured by a photometer. For a constant phosphor loading density, the conversion efficiencies increase significantly (see Fig. 3) when particle sizes change from 2.5 to 10 $\mu$m and somewhat saturate as the particle size is further increased.

#### B. MTF measurements

The spatial resolution of phosphor films is characterized by the modulation transfer function (MTF) which describes the modulation in signal amplitude in the image of a sinusoidally varying object as a function of the object spatial frequency. The MTF, $T(u)$, is given by the modulus of the Fourier transform of the line spread function (LSF), $l(x)$:

$$T(u) = \left| \int_{-\infty}^{\infty} l(x)e^{-2\pi iux}dx \right|.$$
where \( u \) is the spatial frequency of the image. The LSFs of phosphor films were measured at the Sunnybrook and Women’s College Health Sciences Center. The results are depicted in Fig. 4, we see a degradation of spatial resolution as the phosphor film thickness increases. In thicker films, the optical photons generated inside the phosphor film need to travel larger distances to the detectors where they get scattered in the process to increase the isotropy propagation path thereby reducing the spatial resolution.

### IV. INTEGRATION WITH PHOTODETECTORS

The \( \alpha \)-Si:H imaging array considered in this work consists of a two-dimensional (2D) matrix of light sensitive \( \alpha \)-Si:H photodetectors that are switched by an active matrix of \( \alpha \)-Si:H thin film transistors (TFTs) (see Fig. 5). When the array is fully covered by a continuous phosphor film and subject to x rays, the optical photons traversing the phosphor are isotropic to reach adjacent photodetectors where they induce cross talk which degrades the spatial resolution of the imaging array. To avoid the cross talk, a new process using negative photoresist SU-8 has been developed to directly integrate the phosphor material over the photodetector region. The SU-8 is a negative, epoxy-type, near-UV photoresist based on EPON SU-8 epoxy resin (from Shell Chemical).\(^{15,16}\) The SU-8 photoresist used in this experiment was supplied by MicroChem Corp. (NANO SU-8 2000). The photoresist has a very high optical transparency above 360 nm, which makes it suitable for imaging near vertical sidewalls in very thick films. Film thickness over 250 \( \mu \)m can be achieved over with a single coating process. Through a curing process, the photoresist can be permanently left on top of the array to serve as a chemically and thermally stable mold. Figure 6 illustrates such a patterned SU-8 mold for integration of the phosphor. Here, the thickness of the SU-8 is 150 \( \mu \)m. The process for creating such a mold is as follows. First, the SU-8 photoresist is spun on the sample. The film thickness depends on the spin speed and viscosity of the resist. After the resist has been applied to the substrate, a soft bake is then applied to evaporate the solvent and to densify the

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**Fig. 3.** X-ray conversion efficiency of phosphor films as a function of a particle size at the identical surface density for different x-ray source voltages.

**Fig. 4.** MTF of phosphor films as a function of film thickness for a phosphor grain size of 2.5 \( \mu \)m.

**Fig. 5.** Photograph of an \( \alpha \)-Si:H imaging array comprising a 2D matrix of \( \alpha \)-Si:H photodetectors and TFTs.

**Fig. 6.** SEM of patterned SU-8 film of 150 \( \mu \)m thickness.
film. The film is then exposed to UV light (wavelength 350–400 nm) using a conventional photolithography technique. A postexposure bake (PEB) is immediately applied to accelerate the epoxy crosslink. All times used for bake and exposure vary with the thickness of the resist film. After PEB, the sample is placed in pure PGMEA (propylene glycol methyl ether acetate) until the unexposed area is fully developed. The curing process is implemented to further crosslink the epoxy. Finally, the phosphor material is deposited inside the patterned cavities so as to directly contact the photodetectors. Following sedimentation, the phosphor is filled inside the patterned cavities of the SU-8 as shown in Fig. 7.

V. CONCLUSIONS

X-ray phosphor films were synthesized and deposited using Gd$_2$O$_2$S:Tb based composite material along with a sedimentation coating technique. Various Gd$_2$O$_2$S:Tb phosphor grained sizes and film thicknesses were characterized for x-ray conversion efficiency and spatial resolution. The conversion efficiency increases with grain size and the MTF degrades with film thickness. Characterization of the MTF for the different grain sites is currently in progress. In order to reduce the optical cross talk and to solve the intrinsic gain-resolution trade-off of Gd$_2$O$_2$S:Tb phosphor for x-ray imaging applications, we have employed the SU-8 high aspect ratio patterning technology to create a mold for direct cointegration of the phosphor with a photodetector array. Test and characterization of the imaging array is currently in progress.

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