A Scintillator Gd₂O₂S:Pr, Ce, F for X-Ray Computed Tomography

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ABSTRACT

An efficient scintillator Gd₂O₂S:Pr, Ce, X (X = F or Cl) has been developed as a solid-state detector for x-ray computed tomography. Doping with halogen ions has improved the emission efficiency by 30% and doping with Ce reduces afterglow caused by traps in the host, Gd₂O₂S. Hot isostatic pressing of this material in powder form with a trace of Li₂GeF₆, as a sintering aid, resulted in a translucent ceramic scintillator.

An increasing demand for improved image quality of x-ray computed tomography (CT) requires a more sensitive and low-noise detector system. At present the whole-body CT apparatus employs an array of Xe ionization chambers for x-ray detection. Since these ionization chambers have limited x-ray absorbance, there is a demand for solid-state scintillators, which have higher x-ray absorption coefficients. For the scintillator materials, the following properties are also required: (i) a high luminescence efficiency, (ii) a good spectral match between its luminescence spectrum and the photodetector sensitivity, (iii) rise and decay time of luminescence much faster than the response time of the detector system, (iv) negligible afterglow intensity, (v) small scattering of the sensitivity among scintillator elements, and (vi) chemical stability in the ambient atmosphere. The afterglow, when it remains in a subsequent frame, deteriorates the image quality, as does the sensitivity scattering causing noise in an image.

Conventional single crystal scintillators have their own drawbacks. For example, CdWO₄ has a low efficiency, and CsI:Tl is hygroscopic and has a long afterglow. For any doped material, there is a graded impurity concentration in a boule generated during the crystal growth from the melt. This may cause inhomogeneity of the efficiency in the boule and in an array of the elements as well. Attention has, therefore, been turned to powder phosphors with high emission efficiencies, and where large single crystals are difficult to obtain (1, 2).

One promising phosphor is Gd₂O₂S:Pr, which has an energy efficiency higher than the conventional single crystal scintillators, high x-ray stopping power, and a decay time (τ₁/₂ = 5.5 µs) short enough to permit repeated imaging with an interval of 1 ms. Most of this paper reports modifications of the chemical composition, Gd₂O₂S:Pr, to improve the x-ray image quality.

A drawback of the phosphor scintillator is the scattering loss of the emission. In order to solve this problem, the authors have developed translucent ceramics of modified Gd₂O₂S:Pr by HIP (hot isostatic pressing) independently of Royce's method (7) except that a halide flux, typically NaBrF₄, NH₄PF₆, or KCl, is added to the starting materials. The starting materials, Gd₂O₃, Pr₂O₃, Na₂CO₃, K₂PO₄, and the fluxes are thoroughly mixed by ball-milling, charged in an alumina crucible, and fired at 1180°C for 3h. The fired product is washed with deionized water and diluted hydrochloric acid to eliminate all flux. The phosphor thus obtained has a mean particle size of about 9 µm. The addition of Li₂GeF₆ to the starting materials produces a phosphor with a mean particle size of 40 µm when the materials are fired at 1300°C for 6h.

The contents of halogen atoms in the phosphor samples were analyzed by colorimetry of iron rhodanide for Cl and by La-alizarin complexone method for F. In the HIP process, a sintering agent is added to the phosphor powder with 40 µm particle size. This mixture is charged in an iron cylinder capsule, which is, after being sealed off in a vacuum, heated at 1300°C for 10h under pressure of 1900 atm.

The light output of phosphor layers or sintered ceramics is measured under stationary excitation by x-rays (the average energy ~70 keV) or ultraviolet light (wavelength = 254 nm) using a Si photodiode from the front side of the sample. The wavelength of the ultraviolet light corresponds to the fundamental absorption region of Gd₂O₂S.

After pulsed excitation, the luminescence of Pr³⁺ decays nearly exponentially with a time constant characteristic of the optical transition, i.e., about 5 µs for the strongest manifold. This fairly fast decay is, however, followed by a long afterglow at room temperature. The intensity of the afterglow is defined here arbitrarily as the integrated luminescence intensity at 5 ms and later after cessation of a pulsed excitation normalized to the total integrated intensity. The x-ray pulse of 4 ms duration was obtained by a 120 kV rotating cathode-tube with a tungsten target.

Thermoluminescence glow curves were measured by a conventional method with a rate of temperature increase of about 5 K/min. The transient thermoluminescence method is described by Nakazawa (8).

Results and Discussion

Spectral overlap of luminescence with detector sensitivity.——Figure 1 compares the luminescence spectra of Gd₂O₂S:Pr and CdWO₄, a typical single crystal scintillator, with the spectral sensitivity of a Si photodiode. Apparently, the luminescence spectrum of Gd₂O₂S:Pr matches with the spectral sensitivity of a Si photodiode better than that of CdWO₄. The concentration of Pr is 1 × 10⁻³ atom percent (a/o). The spectrum of Gd₂O₂S:Pr hardly varies with the addition of Ce and halogen ions at a level of 10⁻³ or lower atom fraction described below.

Effects of halide addition on the luminescence output.—With the intention of increasing the light output of a phosphor layer, a survey was made on the effects of adding inorganic halides to the starting materials. In the first step, alkali halides, the simplest compounds, were tested. Table I shows the relative values of the luminescence output under 254 nm light excitation and the mean particle size are compared for a series of sodium halides. As much as 9 × 10⁻⁵ mole per 1 mole (Gd₂O₂S:Pr)₀.⁹Na₂O₂S were added to

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Fig. 1. Comparison of the luminescence spectra of Gd$_2$O$_3$:Pr, NaF, and the typical spectral sensitivity of a (a) photodiode (curve a). The luminescence spectrum of CdWO$_4$ (curve b) is also given for reference.

Fig. 2. Relative light output and the mean particle size of Gd$_2$O$_3$:Pr doped with F and Cl ions. The values shown are the results of two separate measurements in 100 different runs with an average error of 2% in each case. The data shown were obtained using 254 nm light.

Fig. 3. Light output of NaF, P, and Cl under x-ray excitation. The average output is 70% of the P concentration shown for 254 nm excitation under an F-doping level of 14.

Table 1. Mean light output and mean particle size of Gd$_2$O$_3$:Pr phosphor. All values are for samples excited at 254 nm using the same excitation conditions, which were then fired at 1100°C for 3h. The light output was determined using 254 nm excitation.

Table 2. Optical transmission for white light and density of various cerams produced by HIP using various sintering aids.
where from a free to continuum 18 as after creation of the correlation of an intensity level of $10^{-4} \sim 10^{-1}$ as low as the panel height. It is important in focusing the afterglow, because if they cause artifacts deteriorating the image quality. It was found that doping of Y can decrease the afterglow at room temperature by one order of magnitude. The effects of Y on thermoluminescence glow curves is shown in Fig. 4. The glow peak around 300 K disappearing causing the afterglow is decreased, while the peak of low temperatures are increased by the Y-doping.

A survey of impurities subjected to glow curve traps has led to the finding that Ce is effective in reducing afterglow, as shown in Fig. 4. Doping of Ce as low as $10^{-4}$ per cent decreases the afterglow intensity by about one order of magnitude. Transient thermoluminescence spectroscopy (TTS) has been used to determine the depths of the three main traps causing the three thermoluminescence peaks at Fig. 5. 0.07, 0.58±0.04, and 0.49±0.01 eV. In Fig. 6, Differential analysis of these traps was plotted against Ce concentration. By Ce doping, all the traps are decreased in density. Approximately the decrease of the traps at 0.07±0.01 eV corresponds to the decrease in the afterglow mentioned above. It may be speculated that traps introduced by Ce has located more deeply in the bandgap, so that the output with an increase in Ce concentration.

When Ce$^{3+}$ is incorporated, it decreases the light output as seen in the literature. The luminescence of Ce in ceramics is not yet found to exist. It is reported that an luminescence peak is detected for Gd$_2$O$_2$S:Ce$^{3+}$ even at 9 K, though, in Y$_2$O$_3$ or Lu$_2$O$_2$S, Ce$^{3+}$ absorbs luminescence of around 3.0 eV at low temperatures 0 K.

Preparation of translucent ceramics by HOF—Extrinsic luminescence may arise from a specular layer of the ceramics is limited by large scattering of light inside the layers. To overcome this disadvantage, preparation of translucent ceramics has been attempted by HOF using a sintering aid. The results of a survey of translucent ceramics are given in Table II. The most effective is La$_2$O$_3$F, with which no scattering of 0% type transmittance at 8 mm thick can be obtained by the addition of 0.1 weight percent SiO$_2$. Even without a sintering aid, high optical transmittance can be obtained by Ce$^{3+}$ doping. Translucent ceramics with 0.1 mm thickness can attain 0% scattering at x-ray sensitivity, while Gd, alone, with a thickness of 1 mm only has as sensitive. The detailed properties of these ceramics are described elsewhere.

**Summary**

A new material, or additive, and sintering process was examined to provide high quality x-ray images for Ce ceramics. Particularly important are the effects of Ce on Ce doping 30 increased the transparency of Ce ceramics, and the effects of Ce and Y in reducing the afterglow. To improve the external light output, preparation of translucent ceramics has been attempted using transmittance by the sintering intensity.

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**Fig. 4.** Thermoluminescence glow curves of Gd$_2$O$_2$S:Pr, with and without F doping (30 ppm) shown by curves a and (b). One can inspect the possibility of these ceramics to bring forth improved resolution and contrast and decreased artifacts of the images.
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Plasma Etching of Ion Implanted Polysilicon

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ABSTRACT

Dry etching of polysilicon doped with phosphorus by ion implantation was studied using a parallel plate etcher and two different etch chemistries (SF$_6$-O$_2$-Ar and SF$_6$-Cl$_2$I$_2$-F$_2$-Ar). These two etch procedures were previously found to result in excellent etching of polysilicon which was doped with phosphorus by solid source diffusion. Large differences in the cross-sectional profiles of ion-implanted polysilicon were found while using the two chemistries. SF$_6$-Cl$_2$I$_2$-F$_2$-Ar chemistry caused sharp notch-like undercut, while the SF$_6$-O$_2$-Ar chemistry exhibited linewidth loss without any notchting. Examples of the cross sections of ion implanted polysilicon are presented in this paper along with a discussion of the possible mechanisms which cause the different cross-sectional profiles in the two etch chemistries. The notchting is explained in terms of the variation in the dopant concentration and in the structure of ion-implanted polysilicon at different depths. The absence of notchting in the cross section of ion-implanted polysilicon etched in the SF$_6$-O$_2$-Ar chemistry is explained by proposing that the interaction of oxygen in the SF$_6$-O$_2$-Ar chemistry with the etched surface makes the chemistry less sensitive to the dopant concentration in the etched material. Results of a simple experiment which support the proposed explanation are presented.

Ion implantation is increasingly used to dope polysilicon gates to obtain lower resistivities and also to control the cumulative time-temperature cycling of VLSI wafers (1-8). In comparison to diffusion-doped polysilicon, implanted polysilicon not only exhibits different electrical and morphological properties, but it also behaves very differently in dry etching. Dry etching of ion-implanted polysilicon was studied using different annealing cycles and two different dry etching chemistries (SF$_6$-O$_2$-Ar mixture and SF$_6$-Cl$_2$I$_2$-F$_2$-Ar mixture). Ion-implanted polysilicon etched very differently in the two chemistries. This paper discusses the problems associated with etching of ion-implanted polysilicon and attempts to explain the observed differences in the etching in two different chemistries on the basis of the properties of ion-implanted polysilicon.

Experimental

Etching procedure.—A parallel plate, single-wafer, high etch rate reactor (Tegal 701) which has been described in detail previously (9) was used in this study. The reactor uses RF power at 13.56 MHz pulsed from the peak power of 250 W to an average power of 100 W with a pulsing period of 4 milliseconds. Two mixtures of etch gases were used for etching silicon: (i) SF$_6$-Cl$_2$I$_2$-F$_2$-Ar with 9% Cl$_2$I$_2$ and 18% argon, total flow 34 sccm, 0.35 torr; and (ii) SF$_6$-O$_2$-Ar with 34% oxygen and 4 percent argon, total flow 27 sccm, 0.6 torr. The selection of these two chemistries was based on the results of our previous studies of etching of solid source-doped, n' polysilicon and of thin silicon films on insulator (SOI) in the fabrication of SOI VLSI devices. These two etching procedures routinely provide optimum etching of fine lines down to a linewidth of two microns (µm) by using a positive photoresist mask. SF$_6$-Cl$_2$I$_2$-F$_2$-Ar mixture provides positively sloped sidewalls and SF$_6$-O$_2$ results in nearly vertical sidewalls.

Sample preparation.—500 nm of polysilicon were deposited on thermally oxidized silicon wafers by low pressure chemical vapor deposition in pure silane at 610°C. The polysilicon films were implanted with a dose of 2 x 10$^{16}$/cm$^2$ of phosphorus at 50 keV and were annealed using two different cycles: 600°C, 30 min; and 800°C, 10 min followed by N$_2$ for a total of 30 min. For comparison, some polysilicon films doped with phosphorus by solid source doping at 923°C for 45 min were also used. All the wafers were etched in a hydrofluoric acid etchant to remove the thin oxide grown in the annealing cycles. A positive resist pattern containing features as small as 2 µm was applied to the substrates.

We will propose that the different sidewall profiles observed in the etching of ion-implanted polysilicon are primarily related to the gradient of doping in the implanted film. Two etching experiments were done to characterize partially the dependence of the etch rate on doping. The first experiment employed 3" diameter n(100) and p(100) C2 silicon wafers uniformly doped with known amounts.