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# Photoluminescence in spray-pyrolyzed CdTe ⊘

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the system is that which surrounds the sources. Furthermore, GaAs layers grown by vapor phase epitaxy (VPE) using AsH<sub>3</sub> have never been reported to have as high purity as those grown in an AsCl<sub>3</sub>-based system. We feel that the high quality of the layers grown here is at least partially related to the predominance of the As<sub>1</sub> specie over the As<sub>2</sub> and As<sub>4</sub> at a cracking furnace temperature of 620 °C. The effect may be one of reduced defect density, as discussed above, and/or one related to the incorporation of impurities at the surface. The picture is clouded somewhat by the impurity apparently introduced by the furnace at higher temperatures. Additional work utilizing a furnace design which would permit the independent variation of the As<sub>1</sub> concentration will be required to clarify the role of As<sub>1</sub>

Nevertheless, it is clear that the use of cracked AsH<sub>3</sub> as an arsenic source has resulted in the growth of highest quality MBE layers ever reported. The donor concentration in the films is dependent on the cracking-furnace temperature, and the dominant impurity is likely to be silicon from the furnace liner. A study of the temperature dependence of the carrier concentration in the low-concentration layers indicates that an additional and unknown donor is also present, which has an activation energy of  $0.030 \pm 0.010$  eV. These initial results also indicate that As<sub>1</sub> may be the preferred arsenic specie for the MBE growth of GaAs, but fur-

ther experiments are required to substantiate this hypothesis.

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### Photoluminescence in spray-pyrolyzed CdTe

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We report very intense photoluminescence in spray-pyrolyzed CdTe at 77 K. We also notice striking similarities in the luminescence spectra, decay, and temperature dependence between CdTe and other thin-film semiconductors, which we interpret in terms of recombination at defect sites in intergranular regions.

PACS numbers: 78.55.Hx, 71.55.Dp, 73.60.Fw

Intense photoluminescence has been reported in various thin-film semiconducting materials, including amorphous Si:H (Ref. 1, 2) and Si:C alloys,<sup>3</sup> and microcrystalline CdS (Ref. 4) and GaAs.<sup>5</sup> We report very intense photoluminescence in spray-pyrolyzed CdTe. We also notice striking similarities in the luminescence spectra, decay, and temperature dependence in many of these thin film materials, which we interpret in terms of recombination at defect sites in intergranular regions.

The CdTe films were fabraicated by spraying a solution of 0.05-moles/liter CdCl<sub>2</sub> and 0.05-moles/l TeO<sub>2</sub> on a glass substrate at 425 °C.<sup>6</sup> The films are about 2  $\mu$  thick polycrystalline CdTe with grain sizes less than 1  $\mu$  and a roomtemperature optical band gap of approximately 1.51 eV.<sup>6</sup>

The photoluminescence spectrum of spray-pyrolyzed CdTe immersed in liquid  $N_2$  (77 K) and excited by 30 mW of unfocused 5145-Å Ar-ion laser light is shown in Fig. 1. For comparison we also show the photoluminescence spectra of crystalline CdTe (Ref. 7) and amorphous Si:H alloy<sup>8</sup> measured under identical experimental conditions. The luminescence spectra of spray-pyrolyzed CdTe (i) is peaked at 1.41 eV, red-shifted from the band gap at 1.59 eV, (ii) has a half width of 0.09 eV, (iii) is almost identical to that of crystalline CdTe, only 400 times more intense, and (iv) has an integrated intensity a factor of 6 greater than that of amorphous Si.



FIG. 1. Photoluminescence spectra of spray-pyrolyzed CdTe, crystalline CdTe and amorphous silicon-hydrogen alloy at 77 K.

The temperature dependence of the luminescence intensity of spray-pyrolyzed CdTe from 77 to 117 K is shown in Fig. 2. The intensity initially increases with increasing temperature, but then rapidly decreases exponentially with a low-temperature exponent of 50 meV and a high-temperature exponent of 240 meV. Over this temperature range, the spectral shape and peak position remain unchanged.

The luminescence intensity increases superlinearly as a function of incident laser power at 77 K, but we believe that this is due to sample heating which increases the luminescence efficiency. As the laser power is increased, the peak of the spectrum shifts to the blue, from 1.39 eV at 1 mW to 1.41 eV at 50 mW. When photoexcited with either 4579 and 6328-Å laser light, the peak of the spectrum is unshifted.

We have measured the luminescence decay of spraypyrolyzed CdTe at 77 K photoexcited by a 100-kW 10-nsec  $3371-\text{\AA N}_2$  laser pulse. The results are shown in Fig. 3 as a semilog plot of the luminescence intensity versus time delay after the laser pulse. Clearly, the decay is nonexponential.

In order to understand the above phenomena, it is useful to compare it to other photoluminescence measurements. There has been extensive studies of single-crystal CdTe at 1.8 K which show sharp (half-width <0.01 eV) free and bound exciton lines around 1.59 eV (Ref. 9); we are not seeing such transitions. In stressed CdTe a broad (half-width



FIG. 2. The photoluminescence intensity of spray-pyrolyzed CdTe as a function of temperature.



FIG. 3. Semilog plot of the photoluminescence intensity of spraypyrolyzed CdTe at 77 K as a function of time after the laser pulse.

= 0.10 eV) luminescence line was observed at 1.41 eV, which was interpreted in terms of defect recombination.<sup>10</sup> In spray-pyrolyzed CdS (and amorphous Si:H) the lumine-scence spectra consists of two (one) broad red-shifted lines that were explained in terms of recombination at defect sites in the intergranular region; in the region between the grains, one would expect a high density of defects, including radiative recombination sites, and a great deal of stress, which would broaden the luminescence line shape.<sup>4</sup> We suggest that this is also the situation in CdTe. This conclusion is supported by the fact that the luminescence intensity is so much weaker in crystalline CdTe, where there are no grain boundaries, only surface states, point defects, and dislocations.<sup>9</sup>

The temperature dependence of the luminescence in amorphous Si:H alloys has a peak at about 50 K and then decreases at high temperatures with two exponential regions<sup>2,11,12</sup>; this decrease in luminescence intensity has been explained in terms of thermally activated diffusion to nonradiative centers. The situation in CdTe is probably the same.

Nonexponential luminescence decay has been seen in amorphous Si:H (Ref. 2) and spray-pyrolyzed CdS,<sup>13</sup> and has been interpreted in terms of localized electrons and holes recombining by radiative tunneling<sup>14</sup>; the nonexponential behavior is due to a distribution of distances between the electron and hole. Again, it is not unreasonable to believe the same is true in CdTe.

The peak positions of the luminescence lines in spraypyrolyzed CdS and CdTe are largely unchanged when the photoexcitation frequency or the sample temperature is varied<sup>15</sup>; this is not the case with amorphous Si:H.<sup>2,16</sup> The shifting of the amorphous Si:H photoluminescence peak has been attributed to populating different portions of a broad distribution of defect energy levels<sup>16</sup>; in contrast, both CdS and CdTe have much narrower distributions. However, we cannot explain the small blue shift in the spectrum when the photoexcitation power is increased.

In conclusion, there are striking similarities in the luminescence characteristics of amorphous Si:H and spraypyrolyzed CdS and CdTe. These similarities are rooted in similar defect sites located in intergranular regions. It might be useful to think of these three materials and probably other thin-film semiconductors as a family of related materials, as for example the way we view single-crystal semicon07 July 2023 01:39:25

ductors.<sup>5</sup> And when considering fabricating a device out of a thin-film semiconductor, for example a solar cell, one would choose one member of this family whose characteristics (bandgap, grain size, cost, etc.) are best suited for the job. And maybe in certain situations, spray-pyrolyzed CdTe will be the desired choice.

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# Saturation effects of cathodoluminescence in rare-earth activated epitaxial $Y_3AI_5O_{12}$ layers

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The intensity of luminescence in YAG, activated with rare-earth ions, shows a nonlinear behavior as a function of incident current density under electron bombardment.  $Tb^{3+}$  or  $Eu^{3+}$  activated samples exhibit deviation from linearity at input power densities exceeding  $10^4 \text{ W/m}^2$ , while  $Ce^{3+}$  luminescence is linear up to the highest power densities studied ( $10^8 \text{ W/m}^2$ ). It is shown that nonlinearity effects, in cases where temperature quenching can be excluded, are caused by saturation of the excited-state population. The results are interpreted in a model which also takes into account excited-state absorption within one activator and energy transfer between neighboring activator ions.

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It is well known that in many phosphors used for display or TV applications the cathodoluminescent (CL) intensity depends in a nonlinear fashion on the input current density.<sup>1-3</sup> It is not always clear in these practical circumstances whether this behavior is brought about by temperature quenching effects or other (intrinsic) phenomena. In the present study thermal quenching is excluded by the use of epitaxial phosphor layers of good thermal conductivity.

We have measured the CL output intensity of epitaxial  $Y_3A1_5O_{12}$  (YAG) layers doped with Ce<sup>3+</sup>, Eu<sup>3+</sup>, or Tb<sup>3+</sup> under excitation with 20-kV electrons. In the Tb<sup>3+</sup> and Eu<sup>3+</sup> cases the activator concentration (x in  $Y_{3-x}RE_xA1_5$   $O_{12}$ ) was varied between x = 0.01 and x = 1. The phosphor

preparation is described elsewhere<sup>4</sup>. The measurements were performed in a scanning electron miscroscope. Beam currents ranged from  $10^{-10}$  to  $10^{-6}$  A, while the spot diameter was varied between 10 and 200  $\mu$ m. This resulted in a power density *P* range of  $5.10^2-2.10^8$  W/m<sup>2</sup>. For decay measurements the beam was deflected; then the rise and decay time (1/e value) of the current on the target is smaller than 100 ns. The optical radiation was collected by a mirror system, transmitted to a monochromator and fed into a photon counting system.

An example of the CL output behavior versus input power density (stationary excitation) is shown in Fig. 1 for two lines in the YAG:Tb (x = 0.32) spectrum and for 550-