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A search for novel thermoluminescent radiation dosimeter media

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HIGHLIGHTS

- ZnS:Mn nanophosphors and CVD diamond films as new TL dosimeter media.
- The TL response of both increases linearly with radiation dose.
- For ZnS:Mn doped to 2 moles of Mn is found to be the most sensitive.
- For CVD diamond films there is a need to adjust parameters such as nanoparticles size.

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ABSTRACT

We describe two example pilot efforts to help define new thermoluminescent dosimeter media. The first concerns ZnS:Mn nanophosphors, prepared by chemical precipitation using zinc and sodium sulfate, doped with manganese sulfate at concentrations varying from 1 to 3 mol. The second concerns chemical vapor deposited diamond, produced as a thin film or as amorphous carbon on a single-crystal silicon substrate, each deposited under the same conditions, use being made of the hot filament-chemical vapor deposition (HFCVD) technique. The gas concentrations used were 1% CH_4 in 99% H_2 and 25% CH_4 in 75% H_2. Characterization of formations used FESEM, XRD and EDX. The nanophosphors consisted of particles of sizes in the range 85–150 nm, the thermoluminescence (TL)-based radiation detection medium giving rise to a single peaked glow curve of maximum yield at a temperature of 250 °C at a heating rate of 5 °C/s. The TL response increased linearly with radiation dose, ZnS doped to 2 mol of Mn being found the most sensitive. Regarding chemical vapor deposited (CVD) carbon, inappreciable TL was found for the resultant ball-like amorphous carbon films, graphite, and the silicon substrate, whereas CVD diamond films showed a promising degree of linearity with dose. For both the ZnS and diamond samples, TL signal fading was appreciable, being some 40% per day for ZnS and > 50% per day for CVD films even under storage in the dark at room temperature, making it apparent that there is need to adjust parameters such as the size of nanoparticles.

1. Introduction

Common TL dosimeter (TLD) materials such as LiF:Mg,Ti (TLD-100) are most often applied in measuring low or high doses. One motivation is that most TLD materials suffer from considerable supralinearity at high doses, reducing the choice of TLD materials for dosimetry applications such as in megavoltage radiotherapy. As such, we are currently seeking materials that offer well-behaved response to allow measurement of radiation doses from moderate doses of a few Gy up to 100 Gy.

As a result of their wide band gap, group II–IV compounds are of interest for phosphor production (Hartmann et al., 1982). Compared to bulk materials, nanocrystalline ZnS are known to have rather attractive characteristics, including their photoluminescence (PL) and thermoluminescence (TL) properties (Wu et al., 2006). Size-dependent effects of nanostructures are expected to bring about novel changes in the electronic, optical and mechanical properties of materials, mainly due to quantum phenomena.

In regard to chemical vapor deposited (CVD) diamond, an attractive insulator in modern high-power electronic and opto-electronic devices (large-area CVDs are now available with thermal conductivities ca. 20 $W\,cm^{-1}\,K^{-1}$) (Descamps et al., 2006), its radiation resistance and tissue equivalence makes it highly interesting for radiation dosimetry. To-date, studies of CVD diamond as TLD materials have tended to focus on TL response as a function of

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doping (Descamps et al., 2006; Barboza-Flores et al., 2007; Nam et al., 1991), comparison between undoped and N doped CVD diamond generally lacking any clear trends in TL yield. Although doping levels due to inclusion of N may have contributed to TL response, direct comparison with undoped CVD diamond is difficult due intrinsic defect levels present in all CVD diamond.

2. Methodology

Chemical precipitation was used to produce ZnS nanophosphor samples, adding $ZnSO_4$ to Na_2S, continuously refluxed to obtain a colloidal form of ZnS. $MnSO_4$ injected into the colloid yielded ZnS:Mn nanophosphors, with samples of 1 M, 2 M and 3 M $MnSO_4$ being prepared in this manner. The physical properties of the nanophosphors have been studied using a field emission scanning electron microscope (FESEM), X-ray diffraction (XRD) and energy-dispersive X-ray (EDX) analysis, providing morphological, structural and elemental analyses respectively. For TL study, the samples were first annealed using step-wise heating of 500 °C, 300 °C and 100 °C, for 30 min per step. Some 30 mg of sample was then irradiated to Co-60 gamma rays from a Co-60 irradiator, providing various doses, read-out being performed using a Harshaw (model 3500) TLD reader.

The diamond films were grown in a conventional hot-filament CVD reactor, the chamber was evacuated to 2×10^{-3} mbar, before performing a hot-filament CVD deposition process. A mirror-polished Si wafer with dimensions of $2\times3\ mm^2$ was used as substrate. With the substrate mounted at about 3 mm below the filament, hydrogen gas was run into the reaction chamber with the filament temperature set at about 1800 °C for 30 min to clean the substrate surfaces. Then, reaction gas of a mixture of H_2 and CH_4, at 1% methane concentration was introduced into the reaction chamber. The total gas pressure was 10 mbar and the filament was coiled tungsten (0.5 mm in diameter) heated in a methane–hydrogen atmosphere. The substrate holder temperature was 650 ± 50 °C measured by thermocouple mounted on the substrate holder and the substrate-to-filament distance was 3 mm. Following 6 h deposition, the methane gas was switched off and then the hydrogen gas was left to flow for 45 min to etch the graphite performed during the process. Again, several techniques have again been used in characterization of the film, including Scanning FESEM to determine the morphology/topography and XRD for crystallographic study of the films. In addition, Raman spectroscopy has been used to determine the quality of the films. For TL studies, the samples were first annealed at 400 °C for 1 h before being irradiated by a Co-60 irradiator and readout as before.

3. Results and discussion

The typical morphology and chemical compositions of the ZnS samples are depicted in Figs. 1 and 2 respectively.

As seen in Fig. 1, the nanophosphors obtained are mostly spherical with diameters in the predominant range 85–150 nm. The presence of Mn is evident in Fig. 2. The typical form of TL glow curve is shown in Fig. 3, an intense broad feature, peaking at ~250 °C, that points to the potential suitability of ZnS:Mn nanophosphors as TLD material. The glow curve shape is typical of semiconductor material (Barboza-Flores et al., 2007). In regard to dose sensitivity, the TL response is linear up to a dose of 100 Gy, the sensitivity increasing with Mn molarity as shown in Fig. 4. Fig. 5 shows a rather poor thermal stability, the results being for irradiated samples kept in a darkened room at room temperature.

The initial fading rate is appreciable, with a 40% loss in signal 1 day post irradiation, with only ~30% residual signal remaining after 4 days. Clearly, to be a useful basis for a radiation dosimeter, the fading rate would need to be reduced perhaps by investigation of the affect of annealing or adding of different rare earth elements. It may also be possible to us the photo transfer thermoluminescence (PPTL) system to provide for a more stable situation, the PPTL technique typically using a UV source to photo-stimulate deep trap electrons into more superficial levels (see for instance, Kharita et al., 1994).

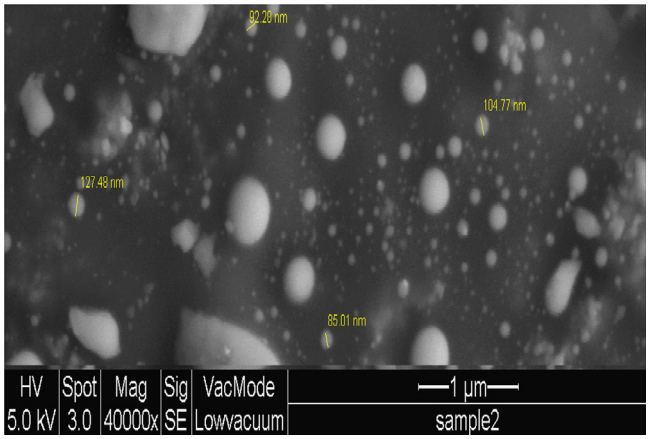

Fig. 1. Micrograph of ZnS:Mn nanophosphors.

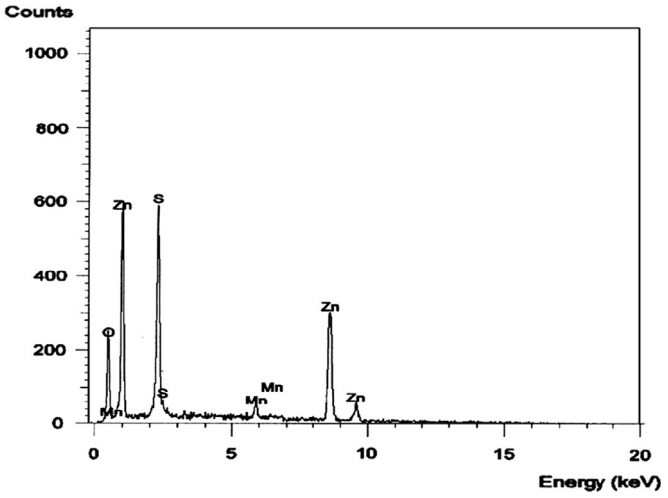

Fig. 2. Elemental makeup of the Mn-doped ZnS nanophosphors.

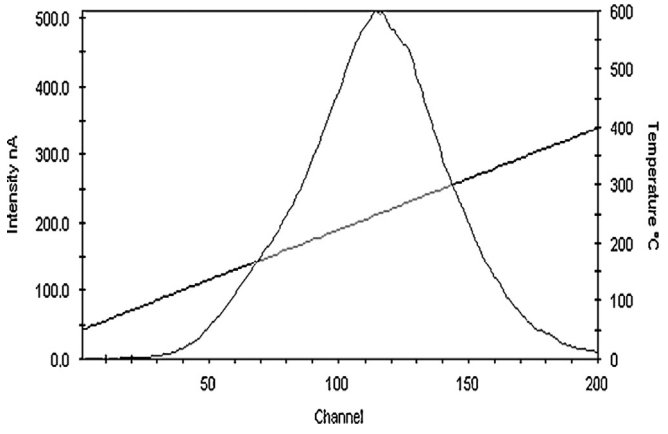

Fig. 3. Typical TL glow curve of ZnS:Mn nanophosphors.