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% CH4 in 99% H2 and 25% CH4 in 75% H2. 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 to be 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.

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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 optoelectronic 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 TL materials have tended to focus on TL response as a function of...
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 ZnSO₄ to Na₂S, continuously refluxed to obtain a colloidal form of ZnS. MnSO₄ injected into the colloid yielded ZnS:Mn nanophosphors, with samples of 1 M, 2 M and 3 M MnSO₄ 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 × 3 mm² 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 H₂ and CH₄, 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).
For the CVD film deposited with 1% CH₄ in H₂ for 6 h, a high diamond nucleation density has been obtained, leading to a continuous film on the abraded silicon substrate. Diamond crystals with rough faces were observed, the crystals size being ~10 μm with an estimated density of 2.25 x 10¹⁰ crystals per cm².

The XRD results from samples obtained using 1% CH₄ in 99% H₂ for a deposition time of 6 h onto a silicon substrate (Fig. 6) shows clear and sharp diffraction peaks of diamond at 43.85°, 75.25° and 91.5° as well as a silicon peak observed at 56.35°. The XRD spectrum for the substrate alone shows the main peak to be at 40.3° due to the SiC (1013) plane giving the interplanar spacing of 2.2383 compared with the published value of 2.2306 from JCPDS standard card nos. 22-1319 and 20-0258.

For TL studies, samples were annealed for 1 h at 400 °C. XRD analysis shows an absence of crystallinity, suggesting that with high temperature annealing, samples become amorphous (Fig. 7). Fig. 8 shows the Raman spectra obtained from CVD diamond on silicon substrates using a probe beam at 532 nm. Fig. 8(a) shows the as deposited CVD diamond where two distinct sharp peaks are evident. The first peak at about 509 cm⁻¹ was due to scattering from crystalline silicon. The second peak at about 1332 cm⁻¹ was the typical Raman shift of crystalline diamond (Staryga and Bak, 2005). The sharp peak which is characteristic single crystal diamond was due to the symmetric bonding of the carbon atoms by strong covalent sp³ bonds, forming a cubic structure belonging to the O₇ (Fd3m) space group. Also barely visible is a small feature at about 1560 cm⁻¹ which can be attributed to amorphous carbon or diamond like carbon (Harshavardhan et al., 1990). These are carbon forms with a mixture of sp² and sp³ bondings, lacking the long range order to form proper crystals. In the spectra for the CVD
diamond sample annealed at 400 °C for 1 h, two broad peaks at about 1360 cm⁻¹ and 1560 cm⁻¹ dominate while the sharp peak due to the silicon substrate also persists. The broad peaks can be attributed to graphitic carbon, characteristic of carbon forms such as graphite and carbon nanotubes (Harshavardhan et al., 1990). The result indicate that the sample has lost some degree of crystallinity due to annealing.

CVD diamond film on silicon substrate is seen to demonstrate linear sensitivity for doses in the approximate range 30–200 Gy, reducing in response beyond that (Fig. 9a). The polycrystalline nature of the films makes the performance of CVD diamond detectors strongly dependent on the film quality (2). A typical TL glow curve is shown in Fig. 9(b).

Fig. 10 shows the fading of CVD film as a function of storage time, when kept in a darkened room at room temperature, being up to ~50% over the period of ~25 h. It is apparent that in its present form the diamond film is unsuitable as a short term TLD, with several factors, such as electron tunneling, that are responsible for the fading (3).

4. Conclusions

The work herein represents two example efforts at producing TL media with unique properties, the first of the media being ZnS nanophosphors. This 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 with 2 mol of Mn was found to be the most radiation sensitive. Regarding chemical vapor deposited (CVD) thin films, 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 found to be appreciable, even with storage in the dark at room temperature, at some 40% per day for ZnS and ~50% per day for CVD films, making it apparent that there is need to adjust parameters such as the size of the nanoparticles.

Acknowledgments

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