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Porous Silicon-Based Quantum Dot Broad Spectrum Radiation Detector

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Abstract

Silicon is a convenient and inexpensive platform for radiation detection, but has low stopping power for x-rays and gamma-rays with high energy (e.g., 100 keV, as used in computed tomography and digital radiography, or 1 MeV, as desired for detection of nuclear materials). We have effectively increased the stopping power of silicon detectors by producing a layer of porous or micro-machined silicon, and infusing this layer with semiconductor quantum dots made of electron-dense materials. Results of prototype detectors show sensitivity to infrared, visible light, and x-rays, with dark current of less than 1 nA/mm².

Keywords

quantum dot; lead sulfide; nanoparticles; porous silicon; x-ray; infrared; light; multispectrum; sensor

1. Introduction

In this paper we present the first application of quantum dots as a direct-conversion radiation detector (in contrast to indirect-conversion materials, e.g., scintillator/photodetector combinations [1]). Our motivation for using quantum dots was to take advantage of the ability of chemists to fabricate radio-dense materials with customized band-gaps, which can theoretically lead to improvements in radio-detector performance. For example, lead sulfide (PbS), which has excellent radiation stopping power (attenuation length of 0.079 cm for 150 keV gamma), has a bulk band gap so low (0.37 eV) that its thermal noise would make it a poor detector choice for high spectral resolution applications. In the quantum dot form, the band gap increases as the size decreases, resulting in less thermal noise. Our rationale for using the composite of the quantum dot form of PbS and silicon was to marry the larger band-gap and high stopping power of the PbS quantum dots with the favorable transport properties of silicon. An additional benefit of the configuration is the possibility of integrating signal amplification and conditioning in the same device.

2. Materials and methods

2.1 Device fabrication

The schematic cross-section of our novel detector is shown in Fig. 1. Device fabrication included the following steps. First, the front of the silicon wafer was made porous. Quantum dots were then cast on the porous silicon. Aluminium electrodes were then deposited on the

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front (porous/quantum dot side) and the back (non-porous side) of the wafer. Finally, wires were connected to the top and bottom electrodes using conductive (silver-filled) epoxy.

The porous silicon [2, 3] was produced by anodizing a highly-doped silicon wafer (n-type, 0.002 Ω -cm, (100)) in an aqueous solution of 6% v/v hydrofluoric acid and 12 % v/v isopropanol (J. T. Baker, Phillipsburg, NJ) at a current of 200 mA/cm² for 3-7 minutes. During anodization the back of the wafer was masked with wax (Crystalbond, Structure Probe, Inc., West Chester, PA). Anodization resulted in pores of 50 – 100 nm in diameter and 20 – 40 μ m in depth, with a 40% volume fraction.

The PbS quantum dots were synthesized under inert conditions using a high temperature solution phase colloidal nanocrystal synthetic route, adapted from Hines *et al* [4], and were isolated and purified in an argon glove box. The crystalline phase, size and morphology of the quantum dots were determined using PXRD and TEM and their optical properties were evaluated using UV-Vis-near-IR and photoluminescence spectroscopy. Using the experimentally determined absorption onset values, band gaps of 1.3 – 1.4 eV were calculated.

Before casting onto the silicon, the PbS quantum dots were re-dissolved in anhydrous hexane at a concentration of 1 g/mL. The silicon substrates were heated on a hot plate to 70°C. 10 μ L of the room temperature solution was deposited on each heated substrate. Casting was done in a nitrogen glove-box (oxygen and moisture free environment) to minimize oxidation. Scanning electron microscopy/energy dispersive x-ray spectroscopy was used to verify that the quantum dots filled the pores (Figure 1B) before progressing to the next fabrication step.

Electrical contacts were made by thermally evaporating 100 nm of aluminum at 10⁻⁶ torr. The front side electrodes are deposited through a shadow mask to produce a circular electrode 7 mm in diameter with a transparent central aperture. We connected wires to the electrodes using conductive silver-filled epoxy. Finally, the prototype detectors were coated in electrical-grade insulating epoxy (MG Chemicals, 832C, Surrey, British Columbia) and removed from inert conditions.

2.2 Detector performance evaluation

2.2.1 X-rays—Our main interest was in the detection of x-rays at energy levels typically employed in medical imaging. We therefore placed the detector in the bore of a clinical CT scanner (Secura, Philips Healthcare, Andover, MA). We illuminated the detector at characteristic energies ranging from 100 to 140 keV and tube currents of 40 – 400 mA for 2 – 3 seconds at a time in single slice mode. The dose delivered during each pulse was in the range of 10 to 100 mGy. The detector was biased at -1.6 V (PbS side with respect to the silicon side) using the circuit shown in Figure 2A. The detector was connected to an operational amplifier (AD 823, Analog Devices, Inc., Norwood, MA) with a feedback resistor of 10 M Ω , resulting in a gain of $\times 10^7$ V/A. The detector and amplifier were battery-powered. The detector, operational amplifier, and batteries were housed inside an aluminum shielding box (with 1 mm thick walls) and were kept at room temperature during the experiment. The signal was sent to an oscilloscope located in an x-ray-shielded area via a coaxial cable (RG 58).

2.2.2 Infrared—Detectors were exposed to a laser source (Model SSL70, Information Unlimited, Amherst NY) with 250 ns pulses of 900 nm infrared radiation (Fig. 2C). Detector output signals were amplified and measured as in the x-ray experiments.

2.2.3 Visible light—The detector was removed from the amplifier circuit and connected to a cyclic voltammogram (Model Autolab PGSTAT 10, Ecochemie, Westbury NY) (Fig. 2D). The detectors were stimulated at room temperature with a white LED (Tikkina 2, Petzl Corp, Crolles, France).

3. Experimental results

3.1 X-rays

The detector response to x-rays is shown in Figure 2B for 100 keV x-rays from a computer tomography (CT) scanner. A linear fit between detector response and x-ray current yields a proportionality constant of 0.095 V/A, with a correlation coefficient $R^2 = 0.98$.

3.2 Infrared

The detector response to pulsed infrared light is shown in Figure 2C (for voltages limited to -0.5 to +2 V), along with the laser trigger trace. The observed detector output has a rise time of 2 μ s and a decay time of 17 μ s. The decay time likely represented the decay time of the amplifier, which has a 10 M Ω resistor, and associated stray capacitance.

3.3 Visible light

An I-V curve generated by a typical detector is shown in Figure 2D showing the change in current when in darkness and when illuminated. The average increase in the detector current at a reverse bias of -1V was 49%.

3.4 Stability

Samples were re-exposed to x-rays, visible and infrared light 12 weeks after fabrication and initial testing, with cumulative exposure in excess of 11 Gy, corresponding to hundreds of CT scans. No variations in response were observed. The detectors were used and stored at room temperature.

3.5 Control experiments

We made two types of detectors for control experiments. One type had porous silicon but did not have PbS quantum dots. A second control set consisted of devices made of non-porous silicon with quantum dots deposited on the surface. In the case where porous silicon was used without PbS quantum dots, the device showed no response to visible light or x-rays. In the case where non-porous silicon was used with quantum dots, there was no response to x-rays, but there was a response to visible light (13 times the dark current).

4. Discussion

By combining desirable characteristics of different materials (i.e., the stopping power of lead sulfide, the charge transport of silicon, low cost for both materials) and excluding undesirable properties (i.e., the low bandgap of bulk lead sulfide), it is possible to design customized radiation detectors.

While the use of sub-micron PbS quantum dots for the detection of visible and infrared light has been demonstrated previously [5], the thickness of these films would not be suitable for detection of high-energy γ - and x-rays (as confirmed in our control experiments). This is illustrated by the fact that the control samples, which have a thin film of PbS, did not respond to x-rays, despite having responded to visible and infrared light. The use of porous or micro-machined silicon (in our case, with thicknesses up to 40 μ m) can increase the effective surface area and thickness of the PbS in order to stop ionizing radiation more effectively. We envision applications of the composite porous silicon/quantum dot platform

technology to large-area flat-panel x-ray detectors, where the increased stopping power could potentially reduce patient dose without compromising spatial resolution. An added benefit of using silicon is the ability to build signal processing and/or amplification structures adjacent to the sensor region, which will likely improve noise-handling and reduce the need for hybridization (e.g., bump-bonding of the sensor to readout electronics) that can limit spatial resolution. The broad-spectrum sensitivity of the composite (i.e., to infra-red and visible wavelengths) may be useful in the design of high-resolution viewfinders.

5. Conclusions

We present the first application of quantum dots used as direct-conversion ionizing radiation detectors. This response was obtained in a composite configuration with porous silicon in order to increase the effective stopping power per detector unit area. The composite detectors are sensitive to a broad range of electromagnetic radiation including infrared, visible light and x-rays. This broadband sensitivity can be tuned for different applications by changing the quantum dot size [6]. The response of the detectors was not degraded despite repeated exposure to light and x-rays.

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Figure 1.

A) Schematic cross-section of the detector, consisting of a silicon wafer with a porous silicon layer which is infused with PbS quantum dots. Aluminum contacts interface with the device on the silicon side and on the quantum dot side. B) Scanning electron microscope with x-ray microanalysis micrograph (SEM/EDS) image of detector cross-section. Silicon (red) and lead (green) overlap in the section where the silicon pores are filled with lead sulfide.

Figure 2.

A) Signal detection circuit. B) Detector response to x-rays, 100 keV, at various levels of x-ray tube current. C) Detector response to infrared (900 nm) laser light. The laser trigger is shown alongside the detector output. D) Detector current vs. applied bias voltage in the dark and under steady, visible light illumination.