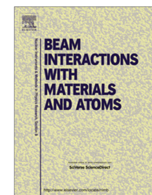
Nuclear Instruments and Methods in Physics Research B 307 (2013) 154–157

Contents lists available at SciVerse ScienceDirect

Nuclear Instruments and Methods in Physics Research B

journal homepage: www.elsevier.com/locate/nimb



Atomic retention and near infrared photoluminescence from PbSe nanocrystals fabricated by sequential ion implantation and electron beam annealing

D.A. Carder [a,c,*], A. Markwitz [b,c], R.J. Reeves [c,d], J. Kennedy [b,c], F. Fang [b]

[a] Industrial Research Limited, 69 Gracefield Rd, Lower Hutt 5040, New Zealand
[b] National Isotope Centre, GNS Science, 30 Gracefield Rd, Lower Hutt, New Zealand
[c] The MacDiarmid Institute for Advanced Materials and Nanotechnology, Wellington 6140, New Zealand
[d] Department of Physics and Astronomy, University of Canterbury, Christchurch, New Zealand

ARTICLE INFO

Article history:
Received 28 September 2012
Received in revised form 13 December 2012
Accepted 16 December 2012
Available online 20 January 2013

Keywords:
PbSe
Lead selenide
Ion implantation
Electron beam annealing
Silicon dioxide
Photoluminescence
Infrared

ABSTRACT

Nanocrystals of PbSe have been fabricated in a silicon dioxide matrix by sequential low energy ion implantation followed by an electron beam annealing step. Transmission electron microscopy reveals PbSe nanocrystals with typical sizes between 3 and 10 nm in the sub-surface region. Rutherford Backscattering Spectrometry has been used to study the total atomic retention, as a function of implanted atoms, following annealing. Photoluminescence was observed in various samples, at 4 K, as a broad peak between 1.4 and 2.0 μm, with observation of a dependence of the peak wavelength on annealing temperature. Room temperature photoluminescence was observed for samples with a high retention of implanted atoms, demonstrating the importance of nanocrystal density for achieving ambient temperature emission in these systems.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

There has been a considerable number of recent experimental and theoretical studies into the synthesis and properties of PbSe nanocrystals [1–9]. This interest is driven by an expectation that nanocrystals of this IV–VI semiconductor will have applications in near infrared photonic devices, including solar cells utilising multiple charge generation from a single photon [4]. In addition this material is, for all practical purposes, the ideal system for studying quantum confinement effects. A large exciton Bohr radius (46 nm), which is shared equally between electrons and holes, allows for strong quantum confinement effects even from relatively large structures [1]. The bandgap of PbSe nanocrystals can potentially be tuned from 0.27 eV (bulk at room temperature) through to around 1 eV for the smallest nanocrystals [5,8].

The synthesis of nanocrystals using ion implantation into glassy materials followed by thermal annealing is an emerging technique [10,11]. In the ion beam synthesis method single, or sequential, atomic species are implanted into a matrix (typically a glassy matrix such as silicon dioxide). As the implanted ions have low or no solubility in the host matrix they are mobile, leading to the nucleation and growth of nanocrystals.

Despite the wide range of nanocrystal materials produced by this method [11] we are only aware of a single publication reporting PbSe nanocrystals [12]. The authors successfully demonstrated single crystal, cubic nanocrystals of PbSe, embedded in silica, with an average size of 3.45 nm. This formed part of a wider study of lead chalcogenide nanocrystals (along with PbS and PbTe). Intriguingly the only material system in the study with measurable photoluminescence was PbS. The absence of luminescence in the case of PbSe was attributed to strong quenching by either photoexcited carriers or surface defect-induced non-radiative transitions. In terms of the latter, a Pb-rich surface layer, creating a high density of mid-gap defect states, has been observed in colloidal PbSe quantum dots [8]. We demonstrate here PbSe nanocrystals formed using sequential ion implantation of Pb and Se into silicon dioxide followed by an electron beam annealing step. The retention of atoms at the subsurface is studied and infrared photoluminescence demonstrated in a variety of samples.

2. Material and methods

Silicon (100) wafers with a 400 nm thermally grown SiO_2 layer were diced into 19 by 13 mm substrates. No cleaning steps were

* Corresponding author at: Industrial Research Limited, 69 Gracefield Rd, Lower Hutt 5040, New Zealand. Tel.: +64 49313100.
E-mail address: d.carder@irl.cri.nz (D.A. Carder).

0168-583X/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.nimb.2012.12.078

performed other than the removal of loose surface debris using an air gun. The substrates were ion implanted with Pb (29 keV) and Se (25 keV) ions sequentially using the custom built ion implantation facility at GNS Science [13]. The samples were implanted under vacuum at 5×10^{-8} mbar in order to avoid surface contamination. The ion beam was electrostatically raster scanned across the surface (at 1 and 10 Hz in lateral directions) to produce lateral homogeneity. The implantation energies and fluence was chosen to achieve, as far possible, overlapping concentration profiles of the two implantation species using calculations from the Dynamic-TRIM software code [14]. The calculated profiles were centered at 22 ± 1 nm, with a FWHM of 20 ± 2 nm. Total fluences ranged from 1.5×10^{15} to 1.5×10^{16} atoms/cm^{-2}, resulting in atomic percentages ranging from 0.3% to 7% for Pb and Se in the matrix. Samples were transferred to an electron beam annealing system [15]. Briefly the annealing is performed under high vacuum ($<10^{-7}$ mbar) using a 20 keV electron beam raster scanned over the thermally isolated sample. The temperature ramping (and cooling) rate was controlled at 5 °C/s through a computer controlled feedback loop. A stable maximum temperature (measured using a 2-colour pyrometer) of 760–915 °C was maintained for 60 min. Although not the focus of this paper this annealing method was chosen since we believe it has the potential to form nanomaterials which are significantly different from other methods [16,17].

The samples were then analysed in cross section using a transmission electron microscope (FEI 80-300 image correction TEM). Further measurements were made using Rutherford backscattering spectrometry (RBS) and using a low temperature photoluminescence system. The RBS was performed using a 2 MeV ($^4He^+$) beam, with further details in [18]. The photoluminescence was performed using an Oxford helium flow cryostat (down to 4 K), ACTON 2150i SpectraPro spectrometer with a 300 line grating and a liquid nitrogen cooled InGaAs detector (extended range cut-off 2.2 μm). An 808 nm diode laser (150 mW), mechanically chopped at 310 Hz, served as the excitation source. To block laser reflections a silicon filter was used at the entrance of the spectrometer.

3. Results and discussion

Shown in Fig. 1(a–c) are cross-sectional TEM images of a sequentially implanted sample, annealed using the EBA method. Fig. 1a shows a cross sectional view of the entire depth of the SiO_2 substrate using a high angle annular dark field (HAADF) contrast mode. In this figure clear nanoclustering of the implanted species is observed with notable features. There is a main band dominated by smaller individual nanoclusters (3–10 nm) distributed from the surface to a depth of around 50–70 nm. Fig. 1(b) shows a number of these nanoclusters and Fig. 1(c) shows a slightly larger (15 nm) individual nanocluster in this near surface region. The majority of the clusters in this region are found to be crystalline with a d-spacing of 0.305, in agreement with the standard PbSe value. TEM analysis of the as-implanted profile (not shown) reveal nucleation of small clusters which are non-crystalline possibly triggered by local heating effects from the implantation process. Interspersed in the near surface region are larger (>20 nm) areas which on inspection appear to be voids from the evaporation of Se during the annealing process Away from the near surface region there are observed to be the occasional larger nanocluster (>15–20 nm), including at the silicon–silicon dioxide interface. EDX analysis of these nanoclusters reveal that they are composed of Se and are probably a consequence of excess Se in the wings of the combined implantation profile (due to a wider implantation distribution for Se over a narrower Pb distribution). Further details of the TEM analysis and high resolution RBS have been discussed elsewhere [19].

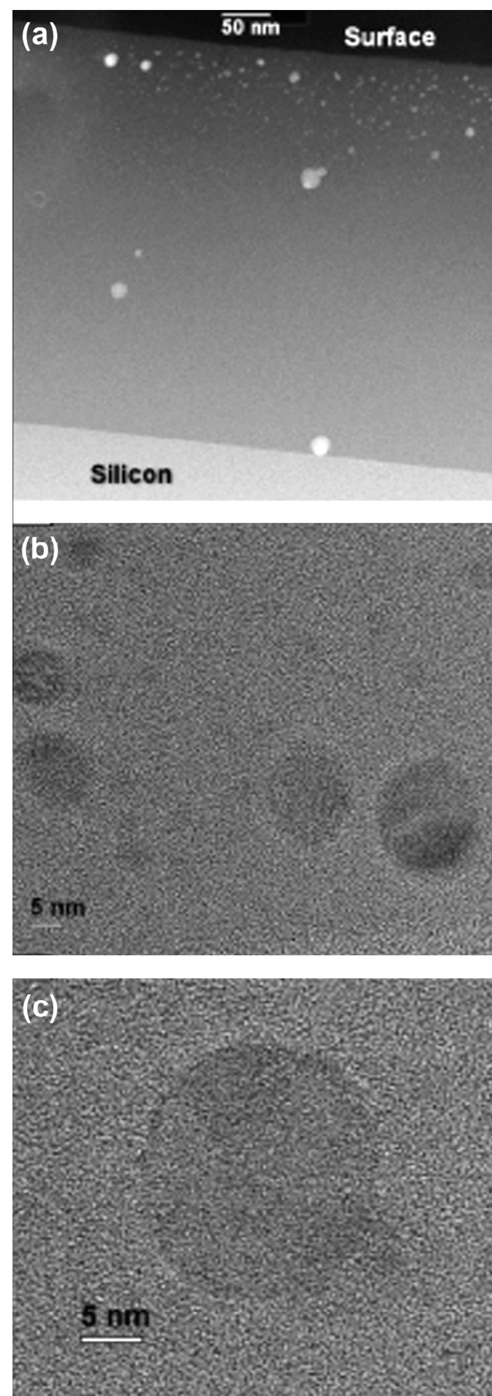


Fig. 1. (a) HAADF-STEM cross sectional image of the Pb + Se implanted and annealed sample. (b) Cross-sectional TEM showing a number of PbSe clusters in the near surface region. (c) Cross-sectional TEM of a single nanocrystal.

The atomic retention of implanted atoms was measured, using RBS, for a range of samples annealed for an hour, at temperatures from 760 to 900 °C. As shown in Fig. 2 the retention of atoms is dependent on the implantation fluence. Below total implantation densities (Pb and Se, atoms/cm^2) of $\sim 10^{16}$ atoms/cm^2 the retention deviates away from unity (i.e. total retention) as a function of increasing fluence. For total fluences above 10^{16} atoms/cm^2 the retention tends back towards unity retention as the fluence increases. Over the annealing temperature range studied the atomic retention is not significantly dependent on temperature. Although the process by which atomic retention proceeds cannot be

Download English Version:

https://daneshyari.com/en/article/1681977

Download Persian Version:

https://daneshyari.com/article/1681977

Daneshyari.com