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Use of Sb spray for improved performance of InAs/GaAs quantum dots for novel photovoltaic structures

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ABSTRACT

Photoluminescence output from InAs/GaAs quantum dots has been improved by a Sb treatment immediately prior to capping with GaAs. Spectra taken at 300 and 80 K show a significant increase in output intensity when the quantum dots are exposed for 15 s under a Sb flux of approximately 0.1 monolayers per second, but this improvement is lost when the Sb exposure is extended to 30 s. There is no significant shift in the emission energies between samples indicating strain relief due to the cap layer is not responsible for the improvement. Analysis of temperature dependent photoluminescence taken between 80 and 300 K show increased activation energies at lower temperatures when an Sb spray is used, suggesting passivation of deep defect levels. For the higher temperature activation energy, corresponding to carrier escape from the QD to the barrier, whilst a 15 s Sb spray gives a substantial increase, the longer 30 s Sb spray sees the activation energy decrease, a result deduced to be due to Sb segregation providing shallow defect levels. A band structure including a very thin GaAsSb layer adjacent to the quantum dots is used to explain these results, with the 30 s Sb spray leading to shallow Sb segregation related defects and a lower activation energy. Depth dependent X-ray photoelectron spectroscopy data support the band structure proposed to explain the photoluminescence results and also reveals the highest concentration of Sb at the sample surface suggesting a 'floating layer' of Sb during growth of the GaAs cap. Some of the implications of these results, for growth of quantum dot samples and for two novel solar cell proposals, the intermediate band and hot carrier solar cells, are discussed.

1. Introduction

Self-assembled (SA) InAs/GaAs quantum dots (QDs) have been the subject of much research interest due to the ability to tailor their structural and optical properties, opening up the possibility for a range of novel optoelectronic devices to be realized [1,2]. Primary amongst these proposed devices has been QD based lasers that promise lower threshold currents that are less sensitive to temperature than bulk and even quantum well lasers [3,4] due to the three-dimensional confinement and delta-like density of states. Photodetectors that detect single photons have also been demonstrated [5] and recently proposals with SA QDs included in photovoltaic devices [6,7] have gained interest with predicted performance superior to conventional devices [7,8]. For two of these proposals, the intermediate band (IB) and hot carrier (HC) solar cells, QD based approaches are being investigated for realizing the specific properties required for efficient operation of these devices.

In the case of the IB solar cell a high density array of QDs is required to form a mini-band to act as the IB, while for the HC solar cell, a high density layer of QDs also forms a mini-band, this time to act as a selective energy contact to the absorber layer. Both require highly uniform QDs for forming a mini-band. A more subtle requirement is that as many of the SA QDs need to be active as is possible, i.e. defects, which act as recombination centers for carriers, must be minimized. Whilst impressive results have been reported for minimizing dislocations formed due to strain energy build-up in structures with a large number of QD layers [8] using strain balanced structures, the problem of local defects close to the QDs, due to the local strain energy remains.

The formation of self-assembled QDs is via the Stranski–Krastanov growth mode where the growth shifts from being two dimensional to three dimensional in order to relieve the strain between the underlying substrate and the material being deposited. When capping the QDs this lattice mismatch is an

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issue as the highly non-uniform strain between QD and cap will lead to the formation of crystal defects around the QD/cap interface [9,10]. These defects act as non-radiative recombination centers, effectively stealing carriers before recombination, and hence light emission occurs or before they can escape the potential well [10].

Previous capping approaches for strain relief have concentrated on shifting the emission wavelength to more applications based values such as 1.3 μm [11,12]. The strain relief means that the lattice strain at the QD/cap interface is lower and so improved performance is seen provided the number of QDs remains relatively the same. In addition to providing a shift in emission wavelength it has been observed that capping InAs/GaAs QDs with GaAsSb instead of InGaAs gives a boost to the light emission for the same strain conditions [13]. This is thought to be due to the Sb acting as a surfactant during the growth of the cap leading to lower interface defect density. It has also been observed that the presence of Sb in the buffer layer also improves the QD/buffer interface again due to the Sb acting as a surfactant [14] and the effect has also been observed for improved interfaces in quantum well samples with very small amounts of Sb [15].

We present results for InAs/GaAs QDs where the QD/cap interface is improved by a Sb spray treatment of the QDs immediately prior to capping with GaAs. Spray times of 0, 15, and 30 s, corresponding to approximately 0, 1.5, and 3.0 monolayers of Sb, show that a 15 s spray gives the best result in terms of output emission with the 0 and 30 s treatments giving similar results to each other. Significantly, no appreciable change in the relative emission energies is seen, implying that Sb soaking of samples may improve emission intensity whilst preserving the desired transition energy. Temperature-dependent photoluminescence results are analyzed in terms of a proposed band structure surrounding the QDs, in which a thin layer of GaAsSb is immediately adjacent to the QDs. The results reveal two main mechanisms for loss of carriers from the ground state levels of the QDs, with the activation energy for escape to the first excited levels being increased with the presence of Sb, suggesting the Sb passivates deep defect levels. For escape of carriers from the QDs to the barriers, a higher activation energy is seen when Sb is present, but a 30 s Sb spray degrades the activation energy in comparison to a 15 s spray, a result we attribute to increased Sb segregation and the non-radiative recombination associated with this. Results from X-ray photoelectron spectroscopy depth profiles support the proposed band structure in the vicinity of the QDs, and also suggest the highest concentration of Sb is at the surface of the two samples subjected to the Sb spray treatment, indicative of a floating Sb layer during the growth of the GaAs cap. Some of the implications of these results for implementation in novel photovoltaic structures are briefly discussed.

2. Experimental

All of the samples studied were grown by molecular beam epitaxy in an AppliedEpi GenIII system on semi-insulating GaAs substrates. Gallium and indium fluxes were supplied by conventional thermal sources with As and Sb fluxes provided by cracker sources (both with valves, though the Sb cracker valve is unable to be closed), providing dimer rich fluxes for both Group V elements. The temperature was monitored by a pyrometer calibrated to a GaAs de-oxidation temperature of 580 °C, determined by observing the reflective high energy electron diffraction (RHEED) pattern. The growth rates determined by monitoring of the RHEED oscillations for GaAs and InAs were 0.4 and 0.035 monolayers/s, respectively, and the measured beam equivalent pressure for the Sb_2 was 9.7×10^{-8} Torr, roughly equivalent to 0.1 monolayers/s, for all samples. The As overpressure for all of the GaAs and InAs growth steps was 2×10^{-6} Torr. All of the samples consisted of a 200 nm GaAs buffer layer grown at 580 °C. After cooling to 500 °C a short 5 nm GaAs refresh layer was grown and following a 10 s rest, approximately 2 monolayers of InAs was then deposited. Three different growth interruption schemes were then employed; sample A had a 15 s rest under As after which the As valve and shutter were closed and the Sb shutter opened for a further 15 s rest giving a total Sb exposure of approximately 1.5 monolayers. The Sb shutter was then closed and the As shutter and valve opened again with growth of GaAs proceeding immediately. For sample B the As shutter and valve were closed immediately at the end of the InAs growth and the Sb shutter opened for 30 s, corresponding to a total Sb exposure of approximately 3.0 monolayers, the Sb shutter was then closed and the As shutter and valve opened with GaAs growth proceeding immediately. Sample C was a control sample with a rest of 30 s under As for the quantum dots meaning no Sb exposure. Fig. 1 provides a pictorial summary of the different treatments employed for the InAs quantum dots following the cessation of the InAs growth. 10 nm of GaAs was grown at 500 °C to cover the quantum dots, for the XPS samples the samples were then cooled and removed for study, for the photoluminescence samples the temperature was raised to 580 °C and a further 60 nm of GaAs grown to complete the samples. The expected difference between the samples with Sb spray (samples A and B) and without (sample C) are summarized in Fig. 2, with an Sb containing compound being formed at the QD/cap interface, the exact nature of this compound is uncertain.

Samples for photoluminescence studies were loaded into a liquid nitrogen cooled cryostat and the spectra were obtained under excitation from a 200 mW continuous-wave 532 nm laser. The luminescence from the PL samples was collected using an iHR320 Horiba Jobin Yvon spectrometer equipped with a TE-cooled InGaAs array. X-ray photoelectron spectroscopy measurements

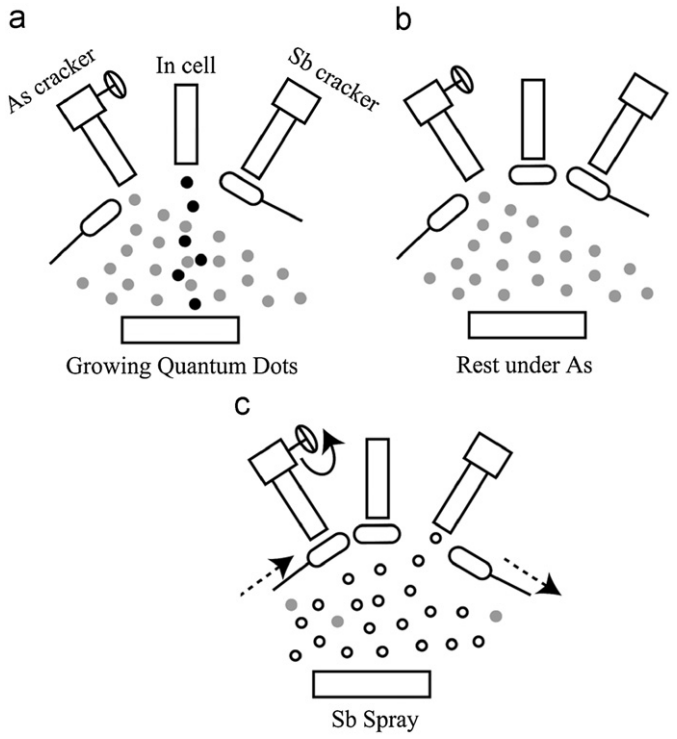

Fig. 1. Brief summary of the different scenarios for the treatment of the quantum dots after (a) growth of InAs, followed by (b) rest under As overpressure, or (c) rest under Sb pressure.