Increasing the quantum efficiency of GaAs solar cells by embedding InAs quantum dots

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Abstract. Development of Metalorganic Vapor Phase Epitaxy (MOVPE) technology of InAs quantum dots (QDs) in GaAs for photovoltaic applications is presented. The growth peculiarities in InAs-GaAs lattice-mismatched system were considered. The photoluminescence (PL) intensity dependences on different growth parameters were obtained. The multimodal distribution of QDs by sizes was found using AFM and PL methods. GaAs solar cell nanoheterostructures with imbedded QD arrays were designed and obtained. Ones have been demonstrated a significant increase of quantum efficiency and photogenerated current of QD solar cells due to photo effect in InAs QD array (0.59 mA/cm² for AM1.5D and 0.82 mA/cm² for AM0).

1. Introduction

Technology to form self-organized InAs quantum dots (QDs) in GaAs was researched intensively within the framework of the Molecular Beam Epitaxy (MBE) technique, which ensures ample feasibilities for controlling the properties of the QD arrays [1]. For light-emitting devices (like lasers, micro-resonators etc.) grown using the MBE, QDs have already demonstrated the improvement of a number of parameters [2, 3]. Recently the great interest for using InAs QDs into the photovoltaic devices have been appeared. The InAs QDs imbedded into GaAs solar cell (SC) allow realizing two important photovoltaic concepts. First of all it is intermediate-band (IB) solar cell [4] which promised to create the equivalent of a triple-junction solar cell in a single-junction solar cell. Secondly, InAs QDs allow obtaining photo-current balance into the high-effective multijunction (MJ) solar cells based on lattice-matched Ga₄₉In₅₁P/Ga₅₉In₄₁As/Ge heterostructure [5] due to extending Ga₄₉In₅₁As subcell spectral sensitivity and thus increasing its photogenerated current. But the growth of SC heterostructures has been widely studied as applied to the Metalorganic Vapor Phase Epitaxy (MOVPE) technique while the technique for the formation of multilayer QD arrays was investigated in detail regarding the MBE. Consequently, the first IB solar cell prototype [6] was made using InAs QDs grown by MB in GaAs SC [7]. The highest efficiency for QD SC achieved by MBE was 18.32% in 2009 [8]. However in all cases the increase in photocurrent obtained due QDs, as compared to a control cell without QDs, is very small and has been accompanied by a reduction in the voltage with an overall reduction in efficiency.
The first successes with QD SC grown by MOVPE was a were demonstrated by [9-11], where QD SCs with an efficiency of 18.7% (AM1.5G, 1 sun) was achieved due to five layers of QDs. The strain-compensation GaP layer technology allow demonstrating in [12] GaAs solar cell, made by MOVPE with InAs QDs, with a higher efficiency (14.3%) than a control cell manufactured without QDs. However, in spite of demonstrated high sub-bandgap photon absorption by the QDs, the spectral dependence of quantum efficiency in GaAs absorption spectral range was not perfect. This paper focuses on the research and development of the formation process of InAs QDs in GaAs matrix using MOVPE technique. The main purpose of this investigation was to obtain high quality GaAs solar cell structure with good spectral response and, at the same time, with a strong sub-bandgap photon absorption by the QDs.

2. Experimental procedure

All experimental and device structures have been obtained using the MOVPE technique on an R&D installation with a horizontal reactor at low pressure (100mbar). Metal-organic compounds were used as sources of Group III elements (trimethylgallium (TMGa), trimethylaluminum (TMAl) and trimethylindium (TMIn)). Arsine (AsH₃) was used as a source of the Group V element (As). Experiments were carried out on (100) GaAs substrates misoriented to the (111) direction by 6º. The main task in the development of epitaxial technology for the GaAs–InAs system is determining the dependence of the InAs growth rate (GR) on the molar flow of In source under various conditions. Solving this problem in such system is not so trivial because of the lattice mismatch between GaAs and InAs materials which makes it impossible to obtain defect free layers on GaAs substrates and subsequently determine the growth rates both by ex-situ and optical in-situ methods [13], which are effective for lattice matched systems. Thus, to find the dependence of the InAs GR on In molar flow we studied the photoluminescence (PL) spectra of InGaAs/GaAs quantum wells (QWs). The growth temperature of QW was varied in the range from 500 to 700°C, In composition “x” was varied from 5% to 30%.

In order to investigate the growth peculiarities of InAs QDs in GaAs matrix the structures for PL and atomic force microscopy (AFM) measurements were grown. There were two types of structures: Al₀.₃Ga₀.₇As/GaAs/GaAs cap/InAsQDs/GaAs/Al₀.₃Ga₀.₇As (a-heterostructure) and uncovered InAsQDs/GaAs/Al₀.₃Ga₀.₇As (b-heterostructure) for PL and AFM measurements respectively. Structures in series of experiments with a-heterostructure were differed by quantity of InAs material, and by GaAs cap layer growth parameters.

To obtain the PL spectra of the a-heterostructures, a 532nm Nd:YAG laser of 350mW power was used as a source of radiation. A study of the surface topography of b-heterostructure was carried out using the AFM method on a Dimension 3100 (Veeco) microscope at room temperature.

3. Results and discussion

Based on the measured PL spectra from described above experimental QW heterostructures, the linear dependences of the ln composition in the InₓGa₁₋ₓAs solid solution on the TMIn/(TMGa+ TMIn) ratio
in the gas phase were obtained in a wide range of growth temperatures from 500 to 700°C (Fig. 1). It was found that In atoms are more effectively incorporated at lower temperatures.

![Figure 1. In concentration in the In$_x$Ga$_{1-x}$As solid solution in relation to the amount of indium in the gas phase at temperatures of (a) 700, (b) 600, (c) 550, (d) 525 and (e) 500 °C. On inset: the dependences of the InAs growth rate on the TMIn molar flow.](image)

Using the obtained data about In composition in the In$_x$Ga$_{1-x}$As solid solution, the InAs growth rates were calculated from the relation:

\[ V_{\text{InAs}} = \frac{V_{\text{GaAs}}x}{1-x} \]  

where \( V_{\text{GaAs}} \) is the GaAs growth rate.

As a result the dependences of the InAs growth rate on the In molar flow were determined for each growth temperature (Fig. 1 on inset). These curves demonstrate that there is no strong influence exerted by the growth temperature on the InAs deposition rate in the range from 500 to 700°C.

These dependences were used for growing heterostructures with InAs QDs. In our work [14] the b-heterostructures grown on GaAs substrate with (100) orientation and different misorientation (2°, 6°, 10°) were investigated and it was shown that 6° allow perfect GaAs underlayer surface planarity. The AFM image for samples grown on GaAs surface with 6° misorientation is presented in fig. 2 a. Statistic data (fig. 2 b) shows the multimodal distribution of QDs by size.

Moreover, PL spectra from b-heterostructures (fig.3) show two states of QDs (marked as QD1 and QD2). Both states are clearly visible on each curve, while QD1 becomes more pronounced with decreasing measurement temperature. The presence of two peaks at different wavelengths may be indicative of the QDs of different sizes. Thus, this proves the effect of the multimodal distribution of quantum dots by size. The optical properties of a bimodal QD array are considered in detail in [15]. The evolution of PL spectra can also be compared with those produced in the articles [16, 17].

In our work [14] the a-heterostructures grown on different condition were studied by PL and growth rate and growth temperature of InAs QDs for 6° misoriented GaAs substrates were optimized. Here we also investigate the influence of GaAs cap layer growth parameters on PL intensity of QDs.
Figure 2. (a) AFM image of InAs QDs with a thickness of 1.7 ML deposited on a GaAs (100) surface with misorientation of 6°. (b) Statistics of QDs distribution by size.

For QD b-heterostructures grown on 6° misoriented substrates at 520°C the conditions under which the maximum PL intensity is observed depend on the amount of deposited InAs material under different growth conditions were found (Fig. 4). It represents a typical case of a Stranski Krastanov growth mode. Quantum dots formation occurs at a certain critical thickness of the deposited material [18]. This critical thickness depends on the difference between lattice parameter of deposited material and matrix. InAs has a quite narrow technological window for forming QDs on GaAs due to the large lattice constant difference. At the optimum critical thickness of the QDs formation the maximum of PL intensity will be observed. For QDs, deposited at sufficiently low growth rate ($V_{InAs} = 0.0625$ ML/s) and covered with 7 nm GaAs cap layer at growth rate of 4 Å/s maximum position of PL intensity corresponds to ~1.7 monolayer of InAs (Fig. 2, b-curve).

Figure 3. PL spectrum evolution with temperature at excitation level of 10 W/cm². GaAs cap layer thickness is 7nm.

Figure 4 – Dependencies of the integrated PL intensity on InAs thickness grown at 0.0625 ML/s with different GaAs cap layer growth rate: (a) – 2 Å/s, (b) – 4 Å/s.
However, we can see that the GaAs cap layer growth rate is very critical factor affecting the maximum PL intensity of QDs. After reducing the growth rate of the GaAs cap layer from 4 Å/s to 2 Å/s the PL intensity significantly increased (Fig.2 a-curve). PL intensity increased by ~60% by reducing caplayer growth rate by half, that indicate the importance of the cap material quality for optical properties of QDs.

The optimal QD growth conditions determined were used for forming multilayer QD arrays (10 and 15 QD layers) and for embedding them into the GaAs solar cell heterostructure (Fig.5). No strain balance layers have been used. So, to avoid the strain, wide spacers of 35 nm have been grown on the GaAs caplayers. Based on the heterostructures grown, control photodiodes according to description presented in “experimental procedure” part have been manufactured.

Spectral dependencies of the external quantum efficiency (EQE) and the reflection have been obtained using such control diodes. As a result, a spectral dependence of the internal quantum efficiency (IQE) for both samples with QD arrays and for reference solar cell without QDs has been determined (Fig.6). In the region below \( \lambda = 880 \text{nm} \), the spectral dependency of the IQE for a QD SC with 10 QD rows (10xQDs) is at the same level as for the reference SC. This indicates the high quality of the GaAs p-n junction embedding 10xQDs layers into the active region even without the application of strain-balance technology. For the QD SC with 15xQDs a slight drop in the IQE in the spectral range below \( \lambda = 880 \text{nm} \) is observed.

The photogenerated current values obtained by integrating the spectral dependence with the IQE in the range of 880nm–1200nm for the heterostructure of a QD SC with 10xQDsc is 0.58 mA/cm\(^2\) for the AM1.5D spectrum and about 0.74mA/cm\(^2\) for that of the AM0. This corresponds to about 0.06mA/cm\(^2\) and 0.07mA/cm\(^2\) per a QD layer for AM1.D and AM0 spectra, respectively, that is the highest value so far achieved in InAs QDs embedded in pure GaAs. For the 15xQD SC, photogenerated current (\( \lambda = 880-1200\text{nm} \)) is 0.59 mA/cm\(^2\) for the AM1.5D spectrum and 0.82 mA/cm\(^2\) for that of the AM0.
4. Conclusions
The peculiarities of the epitaxial growth in the InAs–GaAs lattice-mismatched system were considered and MOPVE technology of InAs QDs growth on GaAs misoriented substrates was developed. The critical influence of the GaAs cap layer growth parameters on InAs QD PL intensity was demonstrated. Using developed technology SC structures with 10 and 15 layers of QDs were grown and control photodetectors were created. These QD SCs show an excellent sub-bandgap photon absorption in QDs (0.59 mA/cm$^2$ for the AM1.5D spectrum and 0.82 mA/cm$^2$ for that of the AM0) without noticeable degradation of quantum efficiency within GaAs spectral range in comparison with reference SC without QDs. We believe that developed MOPVE technology of InAs QDs growth is attractive for improving photocurrent balance in the lattice matched multi-junction SCs and is also useful for IB SCs.

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