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Carrier emission from the electronic states of self-assembled indium arsenide quantum dots

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Abstract

We have used the new technique of high resolution (Laplace) transient spectroscopy to examine the electronic states of ensembles of self-assembled quantum dots of InAs in a GaAs matrix. These have been produced by solid source MBE. We have monitored the s and p state occupancies as a function of time under thermal excitation over a range of temperatures after electrons have been captured by the quantum dots with different Fermi level positions. This can provide more information about the interaction of the dots with the host matrix than is possible with optical techniques and gives new fundamental insights into how such dots may operate in electronic devices such as memory and sensors. The increase in resolution of Laplace transient spectroscopy over conventional experiments reveals quite specific rates of carrier loss which we attribute to tunnelling at low temperatures and a combination of thermal emission and tunnelling as the temperature is increased.

Keywords: Quantum dot; Indium arsenide; DLTS; Tunnellings; Trapping; Electron emission

1. Introduction

Over the last 20 years, there has been a formidable amount of work applied to understanding quantisation effects in wells and dots in a range of semiconductor systems. The vast majority of this work has centred on optical studies (luminescence and absorption) and on transport. There has also been a very strong theoretical input, which has enabled the community to develop a comprehensive understanding of these systems. In recent years, developments in growth techniques have meant that planar arrays of self-assembled quantum dots can be produced with relative ease in lattice mismatched systems by exploiting the Stranski–Krastanow mechanism of strain relaxation [1]. This has led to an explosion of scientific and technological interest which initially has focused on optical properties. Quantum dots exhibit atomic-like features compared to the broadband structures of bulk semiconductors, and so are rather interesting from the point of view of photo detectors and LASERs. In the latter application, the extremely high radiative efficiency of self-assembled quantum dots and the narrow luminescence line structure are very attractive from a technological viewpoint.

However, relatively recently, attention has been drawn to the potential that quantum dots have in data processing and data storage devices, applications which do not necessarily involve optical interactions. In these applications, the key parameters are the mechanism of charge capture by the dot, charge retention and its emission under external stimuli. Some of these parameters can be inferred from optical measurements but a much more appropriate methodology would be to measure these parameters directly and to gain a fundamental understanding of the mechanisms involved. Such an understanding is probably the only route to properly engineered quantum dot memory devices.

Although there has been a spasmodic effort over a long period of time to study the electrical properties of quantum wells (e.g. [2,3]) and quantum dots (e.g. [4–6]), the interpretation of the data is problematic. Perhaps the most fruitful work in the last few years has been effected by growing a plane of self-assembled quantum dots in a semiconductor doped to a level whereby a depletion region formed underneath a Schottky

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barrier could be modulated so that its edge passed through the plane of quantum dots, according to the applied bias. The presence of charge exchange with the dots is observed in capacitance voltage measurements, admittance spectroscopy and perhaps, most fruitfully, deep-level transient-spectroscopy. In this latter technique, the depletion region is made narrow by the application of a zero or low applied reverse bias, under which circumstances the dots have the opportunity to capture carriers and then in the second phase of the experiment the depletion region is extended by the application of a larger reverse bias, so the dots are contained in the depleted region. In the attempt to return to equilibrium charge is released from the dots driven by thermal energy. By conducting the experiment at a range of temperatures and observing the emission rate an Arrhenius plot can be constructed, the slope of which represents an energy.

The interpretation of what this energy means is a far from trivial task. A number of publications have appeared recently, which address this problem. By careful adjustment of the filling level, Engström et al. [5] effected selective filling of the s-like quantised states. Schultz et al. [6] extended this work and included in their interpretation tunnelling from the confined states. In this volume, the statistics of the tunnelling process is considered in much more detail by Engström et al. [7].

The technique of DLTS provides a fundamentally different approach to the study of confined states compared to photoluminescence. DLTS opens up the possibility of studying wells in a one-carrier system, so that at least in principle dipole effects are under control. However, the emission process from which the DLTS spectra derive is rather complex. Fig. 1(i) provides a schematic illustration of the conduction band in the vicinity of the quantum dot. At this stage in the discussion, it should be pointed out that the detail of the system is dramatically affected by the materials and size of the dots and so as a starting point we will consider indium arsenide dots in a gallium arsenide matrix, with dots approximately 10 nm high and 20 nm wide. Such a system is likely to possess 6 quantised states—2 with s-like character and 4 with p-like character. When the dot captures a carrier (in this case, an electron) the bands bend, effecting a Coulomb blockade which makes capture of a second carrier more difficult (Fig. 1(ii)). In the experimental case that we are considering, capture takes place in a neutral region of the semiconductor as represented by (ii) in the diagram, whereas emission takes place in a high field region (within the depletion region) as illustrated in (iii).

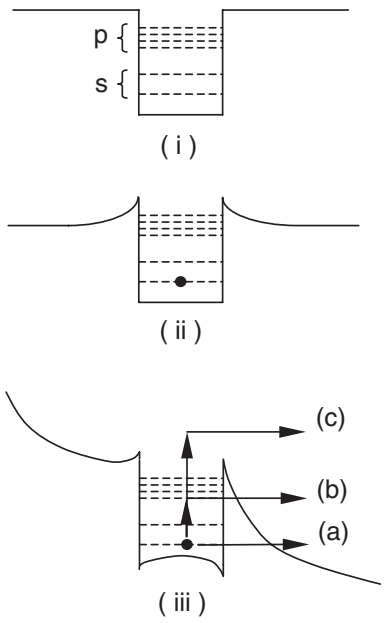

Fig. 1. Illustration of the conduction band in the vicinity of a quantum dot. (i) illustrates the uncharged dot in the neutral region of the semiconductor. The dotted lines indicate the quantised states with s and p character. (ii) shows band bending in the neutral region associated with the capture of one electron at the dot. (iii) illustrates the charged dot in the depletion field (the condition for observing carrier emission) and shows possible mechanisms of carrier loss from the s and p states.

It is evident that there are a number of mechanisms for release that can take place. The most obvious and the one which dominates the thinking of early papers is a simple thermal excitation from the s states to the band. Conceptually, this will result in two peaks in the DLTS spectrum with emission rates which relate to the two s states. However, another alternative is that the electrons are excited to the p states, from which they are then thermally emitted to the conduction band or, as has been mentioned previously, electrons are excited thermally from the s states to the p states and from there they tunnel through the barrier into the band, this is shown as process (b). Process (a) must also be considered and that is the possibility of tunnelling from the s states directly into the band. In all cases, the electrical techniques can only detect charge exchange between the confined states and the band (bound to free transitions) so that rearrangement of charge among the quantised states does not result in any detectable signal using these techniques.

All the above processes could occur but the relative probabilities will depend on temperature, the electric field (which is a function of applied voltage and the carrier concentration of the matrix) and on the matrix and quantum dot materials.

In principle, it is possible to separate the processes using carefully designed thermal emission experiments. However, there are two major obstacles in the experimental realisation of such measurements. The first is that all such measurements to date have been undertaken on ensembles of quantum dots. Unfortunately, the Stranski–Krastanow self-assemble technique, which relies on the relief of strain in lattice mismatched systems, produces a distribution of dot sizes and hence within the ensemble there is a distribution of energies of the quantised states. In luminescence, it is technically possible to examine a single dot and a number of publications have resulted from such work (e.g. [8,9]). Similarly, the absorption spectra of a single dot has also been determined by using refined optics [10] or photoconductivity [11], at the present time the measurement of individual dots has not been achieved using DLTS methods. The second issue is specific to DLTS. Because the technique is a thermally driven process, the energy resolution will be limited to a value of the order of kT, where T is the measurement temperature. However, this is unlikely to

be a problem as the quantised s and p states are separated by a significantly greater energy than kT in the system under consideration. Unfortunately in practice, the resolution of DLTS is limited to a much worse value which revolves around the way in which the measurement is done, essentially it is instrumentation limited. The end result is that the conventional technique is unable to provide a clear separation of emission from the quantised states and some de-convolution of the DLTS spectrum is necessary in order to interpret the result.

The technique described in this paper eliminates the instrumental broadening of DLTS, increasing its resolution by about an order of magnitude over the conventional technique and hence, in principle, providing adequate resolution of the emission rates of carriers from not only the s-like states but also the p states.

2. Laplace DLTS

Over the last 25 years, there has been much effort applied to trying to improve the resolution of DLTS. However, the basic mathematical problem of extracting multiple closely spaced decaying exponential is fundamentally ill posed and has taxed the skills of mathematicians for more than 200 years. Furthermore, the problem associated with DLTS is not simply one of mathematics, the presence of noise, an unknown baseline and a finite length of transient, all complicate the analysis. Recently, Istratov and Vyvenko [12] have reviewed progress in the exponential analysis of physical phenomena.

We approached this problem by designing an isothermal low-noise DLTS system with a highly temperature stable cryostat and applying an inverse Laplace transform and Tikhonov regularisation to separate the exponential. [13,14]. The technique and example results have been described in detail in a recent review [15]. In this way, with transient averaging, it is possible to separate, on a routine basis, transients with more than an order of magnitude better resolution than conventional DLTS, i.e. a time constant ratio of 2:1 for a transient with good signal to noise (~1000:1). In general, for a point defect this means that the concentration of the defect must be more than 0.1% of the shallow doping level but less than 5%. Quite obviously the resolution is degraded if there are physical broadenings such as field dependence of the emission rate or inhomogeneous strain in the sample. Fig. 2 illustrates the difference between conventional DLTS and the Laplace technique for two ideal point defects with very similar emission rates.

In quantum dot samples, our experience is that the signals are sufficiently large for noise not to be an important problem. However if the capacitance transient is more than a few percent of the quiescent capacitance, the exponential transient is distorted by the relaxation of the depletion region and this produces errors in the application of the Laplace transform.

3. Samples

The self-assembled InAs quantum dots were grown using an Oxford Instruments VGSemicon V90H system in a matrix of GaAs doped with Si ($n=2\times10^{16}$ cm^{-3}) using molecular beam epitaxy (MBE) on (100) n^{+}-GaAs substrates at 580 °C for the GaAs matrix and 490 °C for the InAs dots. With a nominal InAs layer thickness of 2.8 monolayers, the Stranski–Krastanow mechanism resulted in dots with a height of ~10 nm and a diameter of approximately 20 nm. Comparison layers consisting of a very thin wetting layer of InAs 1.3 and 1.5 monolayers thick were also grown for comparison. No dots were formed in such layers. GaAs layers without quantum dots or a wetting layer were also grown under similar conditions. The epitaxial layer sequence of a typical quantum dot sample is depicted in Fig. 3. The dot layer is located 400 nm below the Schottky barrier and thus because of the relatively thick upper GaAs confining layers, the dots were subjected to an inadvertent anneal of ~20 min at 580 C. The QD density of 3×10^{9} cm^{-2} was determined by imaging a similar uncapped sample with an atomic force microscopy (AFM) as shown in Fig. 4. Evaporation and subsequent alloying of AuGeNi/Au to the back of the structure formed the Ohmic back contact. Schottky diodes were then fabricated by evaporating Al on the GaAs top layer of a diameter of 1 mm.

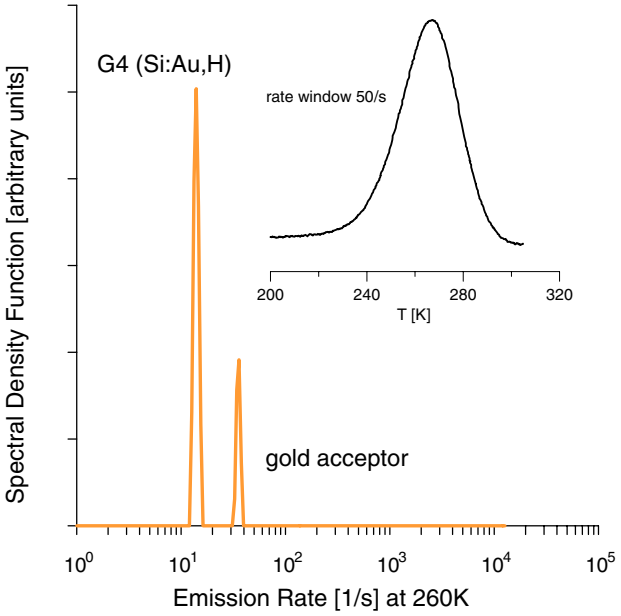

Fig. 2. An illustration of the increased resolving power of Laplace DLTS over the conventional technique, in relation to two point defects in silicon. The inset shows the conventional DLTS scan for a silicon sample doped with gold and hydrogen. There is no indication from the shape or line width that this originates from other than a perfect point defect. The main diagram shows the Laplace DLTS spectra on the same sample where the presence of two similar states, gold and gold hydrogen (G4) is clearly evident.

4. The spectra

We have studied the samples described above with the objective of deciding if Laplace DLTS can provide valuable information over and above the conventional technique. At this stage, we have worked on ensembles of quantum dots and so one of the major problems associated with trying to understand the physics of the behaviour is still with us. In all the samples described, there must be a distribution of size and this obviously is a confusing factor in the interpretation.

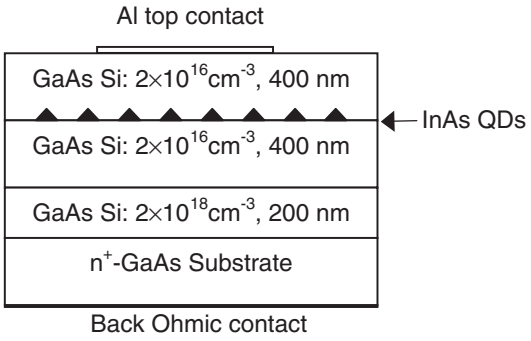

Fig. 3. Schematic of the epitaxial layer sequence of a typical quantum dot sample.

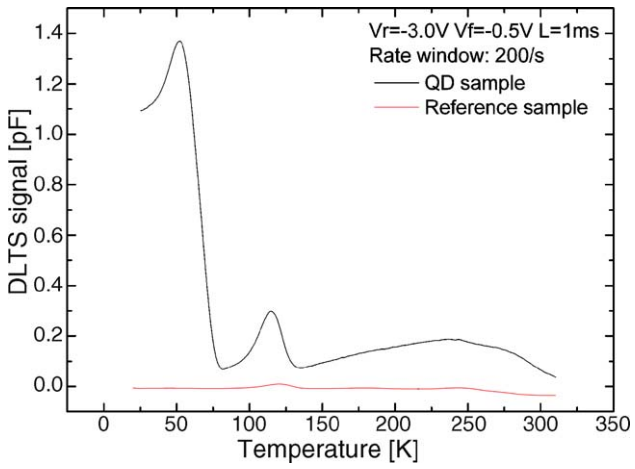

Fig. 5. Conventional DLTS spectra comparing an InAs quantum dot layer in GaAs with a similar structure containing only a wetting layer (1.2 monolayers) of InAs.

Fig. 5 shows the conventional DLTS scan for a quantum dot sample compared to a reference sample containing only the wetting layer, as described above. It can be seen that there are a number of features present in the quantum dot DLTS spectrum, which are not present in the wetting layer spectrum. In particular, the peak at around 50 K with the broad shoulder extending to lower temperatures and a peak at around 115 K, which is broadened on the low-temperature side suggesting that it results from either a non-exponential transient or a number of exponential components. There is also a broad feature at high temperatures, suggesting some sort of continuum of states.

Although comparison with the wetting layer gives some indication as to what features can be attributed specifically to the quantum dots, it is not a definitive guide. Quite obviously the strain distribution in the layers is very different in the quantum dot sample and the reference sample.

It can be seen that in the reference sample, there is a small peak at about 120 K. At higher reverse bias, this peak is much larger, in fact considerably larger than the peak observed in the quantum dot sample. This is likely to be the deep state commonly observed in MBE material referred to as M1 [16]. However, it is evident from the peak position and shape in the quantum dot sample that there are other contributions to the electron emission besides M1 [17]. Some indication of this can be seen from the Laplace DLTS spectra shown in Fig. 6, here we can see very clearly that there are three components to this peak, the behaviour of the three peaks differ considerably. In particular, the magnitude of peak 2 changes rapidly with reverse bias, whereas the change in 1 is minimal over the range shown. In addition, the activation behaviour is significantly different, as we will discuss later. Let us now consider the low-temperature DLTS peak shown in Fig. 5.

Fig. 7 shows the Laplace DLTS spectra taken at 60 K, this provides an insight into the low-temperature DLTS peak. The reverse bias condition is the same as the DLTS measurement of Fig. 5, but a range of filling voltages is used so as to selectively fill the confined states. As was seen in Fig. 2, Laplace DLTS represents the discrete emission rates referenced to perfect exponential as almost delta functions in the displayed spectra. It is very evident in Fig. 7 that there is a range of emission

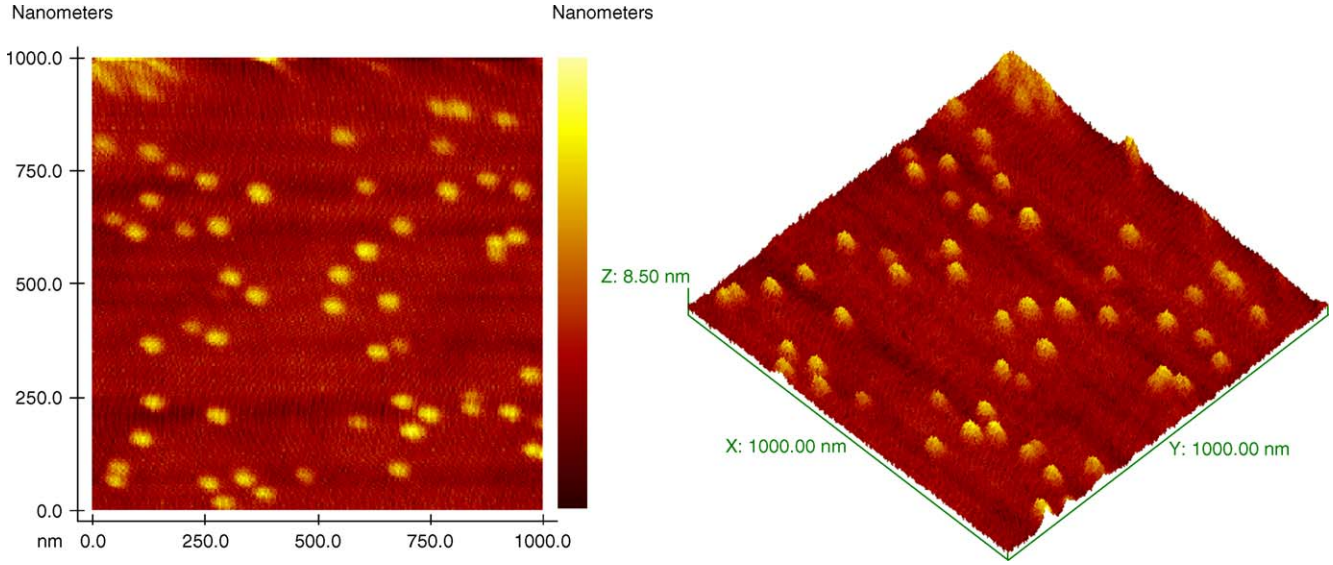

Fig. 4. Atomic Force Microscope image of an uncapped control sample. The image is of an area 1 μm square. The InAs islands are grown on a GaAs substrate and have an approximate diameter of 20 nm and are 4 nm high.

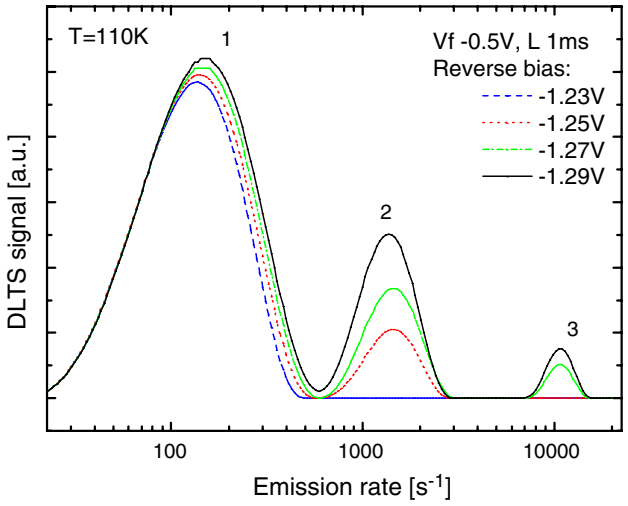

Fig. 6. Laplace transient spectra taken at 110 K of a quantum dot layer. It is evident that there are components originating from deep states as well as a possible contribution from the quantum dots.

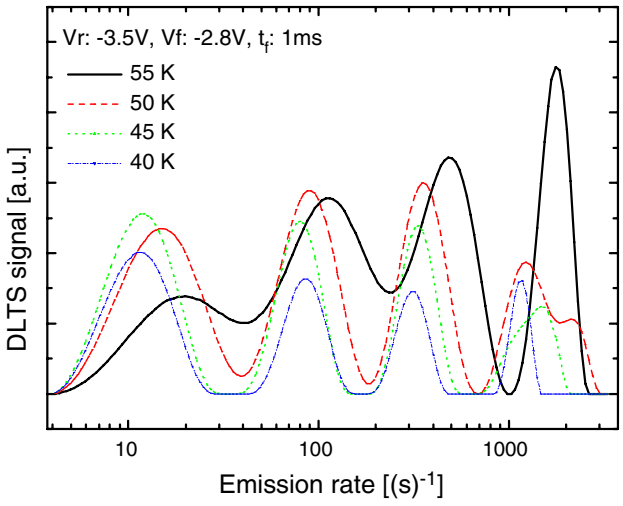

Fig. 8. Laplace transient spectra of quantum dot states at a larger reverse bias than in Fig. 7 and at lower temperatures, conditions in which it would be expected that tunnelling was more significant than in Fig. 7.

rates, which cannot be separated unambiguously. The system is designed to effect the principle of parsimony and so in such circumstances where there is a continuum of emission rates or emission rates that are very close together (about a factor of 2), such broad spectra are generated.

However if the temperature is reduced and the reverse bias increased, detailed structure starts to emerge in the Laplace DLTS spectrum as shown in Fig. 8. Quite obviously, reducing the temperature reduces the probability of thermal emission while increasing the reverse bias increases the probability of tunnelling. In the temperature range between 50 and 55 K, the position of the peaks shifts, i.e. they activate with temperature. However below 50 K, there is no meaningful change in the position of the peaks with temperature, suggesting an athermal process. However, if the peaks are examined as a function of reversed bias, then the emission rate increases with increasing reversed bias.

We conclude from this observation that tunnelling dominates the spectrum. Moreover, this provides strong evidence

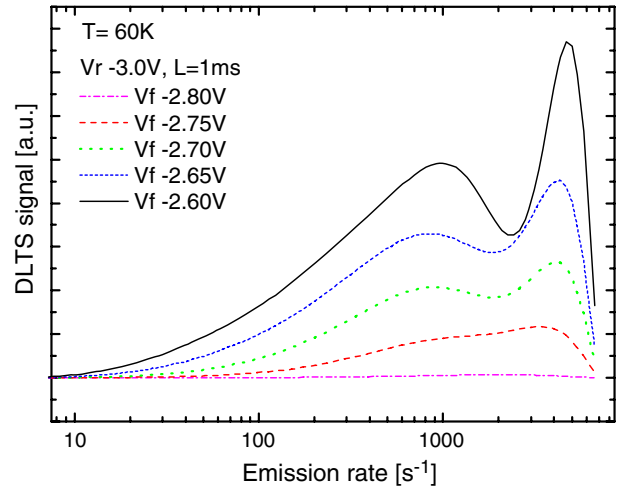

Fig. 7. Laplace transient spectra of the quantum dot states at 60 K obtained by using different filling pulse biases.

that there are a number of discrete tunnelling rates operating in parallel within our sample.

5. What do the spectra mean?

Although Laplace DLTS provides clear and reproducible data on these quantum dot samples, its interpretation is unclear apart from the fact that at low temperatures tunnelling processes appear to dominate, as shown by processes (a) and (b) in Fig. 1(iii). Some additional information can be obtained from quantifying the charge exchange. From the DLTS measurements, we can quantify with considerable precision the charge released to the band, this can be computed from the area enclosed within the peak. In an ideal situation and exercising care in the measurement of all the parameters concerned, this figure can be determined to within a few percent. If we know the dot concentration precisely, and its position within the depletion region, we can then calculate how many electrons per dot the peak represents.

Unfortunately in this case, we do not have a precise measure of the number of dots involved on the samples we studied. Our data are derived from AFM measurements as shown in Fig. 4, where by necessity we are measuring a similar sample but without the gallium arsenide capping layer. However, the comprehensive study of Ledentsov et al. [1], in the same material system with very similar growth conditions, indicates that the dot concentrations will not change dramatically during the capping process. In consequence, if we take the AFM observed value and consider the DLTS spectra of Fig. 5, we can say that if the peak at 120 K emanates entirely from the quantum dots then it represents on average the loss of one electron from three quantum dots. If we then consider Fig. 6 in which a signal, probably due to the quantum dots, is separated from signals, due to deep states, then on average we are removing only one electron from every 30 quantum dots. Considering the lower temperature peak then at 60 K we are removing at least two electrons from each quantum dot.

However, the difficulties of analysing such a complex line shape in conventional DLTS open up the possibility and that as many as five electrons are involved.

Considering now the Laplace spectra taken at 60 K in Fig. 7, then the total spectrum represents approximately two electrons per dot. As the filling conditions are set so as to only fill the s states this is quite consistent with expectations of a combination of thermal excitation and tunnelling.

In Fig. 8, the fact that the five Laplace peaks represent a sequence of discrete electron transfer rates due to tunnelling is quite remarkable. It seems highly unlikely that this is anything to do with the energy levels of the s or the p states in the well. The energetic separation of s1 and s2 is generally calculated to be rather small as is the separation of individual p states. The energy difference between the two groups in this system is expected to be about 80 meV. The emission rates are independent of temperature but dependant on the field. As it seems likely that there is a size distribution of the dots, the mechanism is probably more associated with the amount of charge on the dots rather than on the energies of the quantised states. A possible hypothesis is that due to the band bending the tunnelling rate is dependant on the charge state of the dot, so that if the dot is highly charged and the band bending severe, the tunnelling rate is high and in consequence represents the loss of the first electron [18]. When the electron is lost from any particular dot, the band bending changes and the tunnelling rate decreases. This would explain the sequence of discrete tunnelling rates, and, as the coulombic field extends well beyond the physical size of the dot, would be independent of the dot size.

It would seem that in our samples the process occurring at 120 K is a very minor contributor to the carrier loss mechanism, perhaps representing thermal excitation from the s states to the band. This is a rather different situation to that reported previously [5,6]. However, there are significant differences in the samples, specifically in the doping level of the material. Our samples have a doping level almost an order of magnitude greater than those of Schultz et al. [6] and more than twice that of Engström et al. [5], so that it seems likely that the higher field in our samples could be responsible for a greater significance of tunnelling. In order to try to understand the difference, samples from these two groups are being measured using Laplace DLTS but at the present time no conclusive results have been obtained.

6. Conclusions

This paper does not pretend to be anything more than a preliminary look at the application of Laplace transient-spectroscopy to quantum dot structures. However, it does seem that the technique has the potential to provide information that is difficult or perhaps impossible to obtain by other methods. The initial measurements have revealed an intriguing phenomenon namely the presence of a range of discrete tunnelling rates from the dot. All these measurements have been done on ensembles of quantum dots and preliminary indications are that if the Laplace technique is to be valuable for examining thermal emission processes, it is important to develop a methodology to look at individual dots as has been proved necessary in luminescence and absorption.

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