RELATÓRIO TÉCNICO FINAL

Número do processo: CEX-2154/06

Modalidade: Edital Universal

Título do projeto: Caracterização óptica de nanopartículas semicondutoras utilizando microluminescência resolvida espacialmente

Coordenador: Adamo Ferreira Gomes do Monte

Área (sub-área): Física (Matéria Condensada)

Instituição: Instituto de Física, Universidade Federal de Uberlândia

Início: 02/01/2007 – Término: 02/01/2009

UBERLÂNDIA-MG, Outubro 2008.
1. Introdução

Este relatório se refere aos resultados obtidos durante o período de aproximadamente 20 meses de pesquisa iniciada em janeiro de 2007, no Grupo de Óptica e Fototérmica (GOF) do Instituto de Física da Universidade Federal de Uberlândia. Ele visa dar uma visão geral dos trabalhos que foram realizados, e que outros que ainda estão em andamento. Em anexo, incluímos os artigos científicos publicados.

Neste projeto, realizamos a instalação e o aprimoramento dos equipamentos utilizados para a montagem da microluminescência. Desenvolvemos as atividades de pesquisa, quais sejam as de realizar cálculos numéricos e simulações voltadas para análise da microluminescência, preparamos e processamos as amostras para caracterização e caracterizamos os sistemas nanoestruturados disponíveis no laboratório. Integramos a equipe dentro do projeto de pesquisa para desenvolver e, possivelmente, transferir tecnologia para o sistema produtivo. Publicamos trabalhos na temática do projeto em revistas internacionais indexadas. Apoiamos o nosso programa de Pós-Graduação em Nanociência da UFU e trabalhamos na formação de recursos humanos: iniciação científica e mestrado, dentro da especificidade do tema proposto no projeto. Os resultados também foram apresentados e publicados em conferências nacionais e internacionais.

2. Descrição da proposta inicial do projeto

O estudo de nanopartículas com diâmetro entre 1 e 20 nm tornou-se uma grande área interdisciplinar de pesquisa nos últimos anos. Este é um assunto atualíssimo e de grande importância científica e tecnológica. Um dos fatores que atraem tanto interesse para a pesquisa de nanopartículas é a necessidade de minituarização de dispositivos óticos e eletrônicos. Os processos de transferência de energia também são de máxima importância em física básica. Podemos lembrar que é um dos mais estudados fenômenos na natureza, como ocorre no processo de fotossíntese. A fim de tratar desses assuntos, o objetivo principal deste projeto é voltado para a implementação de uma técnica especial no Estado de Minas Gerais com a finalidade de obter focalização e manipulação óptica micrométricos, aliado a baixas temperaturas, para caracterização de materiais nanoestruturados no campo da
física da matéria condensada. Conseqüentemente, a chamada técnica de varredura da microluminescência será utilizada para determinar os processos de difusão e transferência de energia em materiais luminescentes, como as nanopartículas semicondutoras.

3. Trabalhos realizados

Iremos demonstrar o embasamento de alguns estudos que foram realizados utilizando-se principalmente a técnica de varredura espacial da microluminescência. São temas relacionados com ao estudo de nanopartículas e pontos quânticos, os quais foram selecionados para este relatório.

3.1 Medida de microluminescência resolvida espacialmente em Pontos Quânticos (PQs) de InAs-AlGaAs

Estamos estendendo este trabalho para InAs crescido em um matrizes de Al_xGa_{1-x}As para vários valores de x. Aumentando a composição x de Al irá aumentar o confinamento do potencial, modificando tanto o nível de energia da estrutura quanto os mecanismos de escape de portadores. Então, a fotocorrente e a microluminescência são usadas para estudar estas propriedades. Pontos quânticos de InAs-AlGaAs possuem novas aplicações em dispositivos lasers, onde o aumento do confinamento permite aumentar a operatividade da temperatura. Utilizando a microluminescência excitamos uma pequena região da amostra (~1μm), excitando assim poucos pontos, ou seja, estamos mais próximos de estudar a dinâmica dos elétrons quando eles se encontram confinados em um único ponto quântico. O tempo de vida de recombinação do estado fundamental para os PQ’s de InAs tem sido medidos em 1ns, enquanto que o tempo de vida dos estados excitados são menores (~ 30ps sob alta densidade). A habilidade de se medir diretamente as larguras de linha fundamentais permite um estudo sólido dos efeitos de espalhamento de portadores, dephasing e relaxação do tempo de vida do estado fundamental e excitado em pontos de InAs.

3.2 Efeitos de campo elétrico na difusão de portadores em pontos quânticos de InAs-GaAs

O objetivo é estudar a estrutura dos níveis de energia e os mecanismos de escape de portadores em PQs de InAs-GaAs com grande confinamento quântico. Com
uma única camada de pontos alojados na região intrínseca de uma estrutura de diodo (p-i-n), os portadores podem ser excitados ressonantemente nos pontos e podem então sofrer recombinação radiativa, ou podem também escapar dos pontos onde eles são coletados na forma de uma corrente elétrica. Tipicamente o diodo é operado sob corrente invertida (reverse bias) que pode ser modulada a fim de estudar os efeitos do campo elétrico nas propriedades ópticas interbandas. Isto tem permitido estudar detalhadamente o efeito Stark quântico-confinado e os mecanismos de escape de portadores em PQ’s. Tipicamente, um espectro de fotocorrente demonstra 3 ou 4 transições ópticas interbandas nos PQ’s. Por exemplo, em pontos de InAs-GaAs tem sido mostrado que o escape ocorre pelo tunelamento a baixas temperaturas e por excitação térmica a altas temperaturas. Utilizando a varredura espacial da microluminescência observamos um comportamento assimétrico da difusão de portadores na estrutura de pontos quânticos. Um comportamento assimétrico foi observado devido ao arraste dos portadores com a aplicação do campo elétrico. Mesmo sem a aplicação do campo elétrico pode-se verificar a assimetria da difusão. Evidentemente a assimetria estava relacionada com os contatos da amostra. Através deste experimento podemos determinar a influência do acúmulo de cargas na estrutura de pontos.

3.3 Transferência de energia em pontos quânticos de PbS

Os processos de transferência de energia em nanocristais de PbS em matriz vítrea foi estudada em função da temperatura e da energia de emissão do ponto quântico. As medidas de microluminescência resolvida espacialmente revelam diretamente uma taxa de transferência que dependente da energia dos excitons, assim sendo a energia é transferida dos pontos menores para os maiores via acoplamento eletrônico. Para isso foram usadas três amostras que continham diferentes tamanhos de nanocristais. Baseando-se nestes resultados podemos melhorar a distribuição de tamanhos dos pontos.

3.4 Photocorrente e spintrônica em pontos quânticos

O uso de uma photocorrente aplicada ao estudo de pontos quânticos auto-organizados é a forma controlar a densidade de cargas dentro dos pontos. Estudos recentes têm demonstrado uma forma de controlar spin de elétrons em pontos
quânticos utilizando campo elétrico. O \textit{spin} de um elétron ou um buraco em um ponto quântico é muito importante para determinar as propriedades eletrônicas e ópticas. Sua manipulação tem grande potencial em spintrônica e processamento quântico de informação. Pode-se identificar mecanismos fundamentais da dinâmica de elétrons e buracos em pontos quânticos auto-organizados de InAs/GaAs sujeitos a campos elétricos verticais utilizando medidas de fotocorrente e PL em função da voltagem aplicada. A amostra de interesse é fabricada por MBE, crescida em uma estrutura de diodo \textit{p-i-n} de GaAs contendo de uma a cinco camadas de pontos de InAs separados por 20nm de GaAs. Elétrons e buracos armazenados afetam fortemente as propriedades eletrônicas e ópticas dos pontos quânticos. Experimentos detalhados de fotocorrente dependente da potência sob excitação ressonante exibem comportamentos \textit{marcadamente diferentes} como função do campo elétrico aplicado. Observam-se claramente saltos na fotocorrente como função da intensidade de PL em função da voltagem aplicada, correspondendo a mudanças na população de excitons. Analisando este comportamento, existe um mecanismo de \textit{spin-flip} envolvendo troca de \textit{spin} com o mar de Fermi nos contatos do dispositivo. O processo de \textit{spin-flip} é revelado na dinâmica de fotocorrente quando a população de exciton aumenta com corrente reversa. O efeito pode ser observado no aumento da intensidade de PL (microluminescência) que demonstra o aumento de excitons claros. Argumenta-se que o exciton escuro tornar-se claro quando o processo de \textit{spin-flip} ocorre no ponto quântico. Este efeito permite controlar o processo de \textit{spin-flip} através de uma voltagem dc.

3.5 Microesferas poliméricas

Estudar a luminescência associada a microesferas poliméricas de estireno-divinilbenzeno (Sty-DVB) dopadas com pontos quânticos (ex.: CdS e PbS) e seu potencial de aplicação como material fotônico. As microesferas funcionam como uma cavidade óptica (microcavidade), cujo espectro de emissão demonstra diversos picos que são associados aos modos da cavidade (\textit{whippering-gallery modes}). Estudar esses espectros de emissão será importante no desenvolvimento de microcavidade laser. A microluminescência entra neste trabalho porque as microesferas têm diâmetros de poucos microns, sendo necessário um feixe de laser mais focalizado. Por isso, usamos a microluminescência paraexcitar e capturar o sinal das microesferas.
3.6 Transferência de energia em nanocristais e pontos quânticos semicondutores

A técnica de microluminescência tem sido utilizada para demonstrar e estudar os processos de transferência de energia aplicados a nanocristais e nanopartículas luminescentes. Inicialmente a técnica de microluminescência mostrou-se adequada para o estudo do mecanismo de migração de fótons em cristais luminescentes. De uma maneira análoga, observou-se o processo de transferência de energia em vidros dopados com íons terras-raras de Nd$^{3+}$. Além da aplicação desta técnica para estudar a difusão de fótons, ou o mecanismo de transferência de energia em cristais dielétricos, foi possível estudar a difusão de portadores fotoexcitados em materiais semicondutores. Os mecanismos de transferência de energia predominantemente em uma amostra com pontos quânticos de PbS foram estudados através do perfil espacial de intensidade de PL. A largura da difusão espacial para baixas energias é maior do que para altas energias, indicando a transferência de energia dos pontos quânticos menores para pontos maiores. Estudos similares da transferência de energia espacial indicaram a ocorrência de um processo de emissão espontânea amplificada (ASE) em pontos quânticos auto-organizados de InAs/GaAs.

De uma forma geral podemos resumir as atividades realizadas através do seguinte cronograma:

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<tr>
<th>Janeiro-Junho</th>
<th>Montagem da técnica de microluminescência;</th>
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<td>Obtenção de dados experimentais;</td>
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<td>Transferência de energia em nanocristais e pontos quânticos semicondutores;</td>
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<td>Medida de microluminescência resolvida espacialmente em Pontos Quânticos (PQs) de InAs-AlGaAs;</td>
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<tr>
<td>2007</td>
<td>Congresso: XXX Encontro Nacional de Física da Matéria Condensada, 2007;</td>
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<td>Congresso: 13 Brazilian Workshop on Semiconductor Physics, 2007, São Paulo. 13 Brazilian Workshop on Semiconductor Physics, 2007;</td>
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## Julho-Dezembro 2007
- Photocorrente e spintrônica em pontos quânticos;
- Transferência de energia em pontos quânticos de PbS;
- Congresso: The International Conference on Surfaces, Coatings and Nanostructured Materials, 2007, Portimão;

## Janeiro-Junho 2008
- Obtenção de dados experimentais:
  - Microluminescência resolvida espacialmente em Pontos Quânticos de InAs-GaAs – influência do campo elétrico;
  - Microesferas poliméricas;
- Congresso: XXXI Encontro Nacional de Física da Matéria Condensada, 2008, Aguas de Lindóia;
- Congresso: The 15th International Conference on Luminescence and Optical Spectroscopy of Condensed Matter (ICL 08), 2008, Lyon;

## Julho-Dezembro 2008
- Obtenção de dados experimentais:
  - Efeitos de campo elétrico na difusão de portadores em pontos quânticos de InAs-GaAs;

### PRODUÇÃO BIBLIOGRÁFICA – Ano 2007


PRODUÇÃO BIBLIOGRÁFICA – Ano 2008


Artigos aceitos para publicação:


4. Conclusões

Comparando o trabalho realizado com o programa inicial, podemos afirmar que este trabalho de pesquisa foi realizado dentro do programa proposto. Além dos experimentos que constavam no cronograma inicial, realizamos novos experimentos com amostras de pontos quânticos em matrizes de vidro, requerendo até mais tempo para a complementação dos trabalhos que estavam na proposta inicial. Sobre a técnica de microluminescência uma das principais vantagens é que ela pode ser usada para qualquer material luminescente, podendo inclusive ser aplicada ao estudo de outros
sistemas, como polímeros, semicondutores orgânicos, etc. Os resultados são bastante satisfatórios e irão permitir a publicação de vários artigos. É também importante ressaltar que durante o projeto vários trabalhos foram apresentados em congressos nacionais e internacionais. Em suma, enumeramos os nossos resultados:

(1) Implementamos a infra-estrutura instrumental e material da técnica de caracterização óptica baseada na microluminescência;

(2) Desenvolvemos as atividades de pesquisa, quais sejam, as de realizar cálculos numéricos e simulações voltadas para análise da microluminescência, preparar e processar amostras para caracterização e caracterizar os sistemas nanoestruturados disponíveis no laboratório;

(3) Integramos a equipe dentro do projeto de pesquisa com os objetivos de pesquisar, desenvolver e, possivelmente, transferir tecnologia para o sistema produtivo;

(4) Publicamos trabalhos na temática do Projeto em revistas internacionais indexadas;

(5) Apoiamos o programa de Pós-Graduação em Nanociência da UFU e trabalhos na formação de recursos humanos: iniciação científica e mestrado, dentro da especificidade do tema proposto no projeto;

(6) Participamos e apresentamos trabalhos em conferências nacionais e internacionais;
5. Referências bibliográficas


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Mean free path for excitation energy migration in Nd$^{3+}$-doped glasses as a function of concentration

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The energy-transfer process and the related migration mechanism of excitation energy, important in the optical dynamics of Nd-doped glasses, were investigated. In order to study the migration mechanism and transfer process, Nd$^{3+}$-doped oxide glasses were produced with doping concentration (N) ranging from 0.1 to 1.9 wt % as Nd$_2$O$_3$. A microluminescence technique was used to measure the spatial distribution of the emitting light as a function of the distance from the center of the laser-excitation spot with different Nd$^{3+}$-ion concentrations. Efficient long-range migration of excitation energy of Nd$^{3+}$ ions was observed at 1.1 wt % of Nd$_2$O$_3$. The critical distance between Nd$^{3+}$ ions, estimated from the observed migration length, shows that dipole-dipole interaction is not the dominant mechanism for energy transfer. The mean free path for migratory excitation energy in the investigated material, assisted by absorption and scattering by defects or phonons, is the most probable mechanism for energy transfer.

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The optical properties of rare-earth-doped dielectric solids have been extensively investigated. In particular, the use of rare-earth ions emitting in the optical-fiber spectral region has attracted considerable interest in applications of luminescent materials. Due to their potential applications for efficient lasering and frequency upconversion processes the investigation of optimized doped glasses requires a substantial effort.

Photon migration has been used to study many material systems, such as polymers, dielectric crystals, semiconductor heterostructures, biological material, and other random media. In order to probe the luminescence source distribution in a diffusive medium, one usually makes use of diffusive light. Within the transport theory the propagation of light in a material medium can be described through a mean free path (L) that determines the average distance the photon travels throughout the system before it is quenched. The extent to which information can be extracted from this approach obviously depends upon the accuracy with which one can model the photon migration by means of multiple scattering. Complete characterization of the optical properties of a particular material is important not only for technological reasons but also for obtaining a better understanding of the energy-transfer process involved.

In this study, we have carried out an experimental investigation of Nd$^{3+}$-doped glasses to evaluate the photon migration mechanism and the strength of the coupling between Nd$^{3+}$ ions by analyzing the spatially resolved microluminescence on the sample surface. In order to perform this study Nd$_2$O$_3$-doped oxide glasses were synthesized with Nd$_2$O$_3$ concentration (N) ranging from 0.1 to 1.9 wt %. The photon effective diffusion length (L$_{eq}$) as a function of Nd$_2$O$_3$ concentration was obtained and used to determine the strength of the interaction between Nd$^{3+}$ ions. By measuring the photon effective diffusion length, we investigated the energy-transfer process that characterizes each sample. The spatial distribution of the luminescence was studied and the energy-transfer processes among Nd$^{3+}$ ions were discussed. Using the microluminescence data we can also understand the quenching mechanism observed at the higher end of the Nd$^{3+}$-ion concentration in the analyzed materials.

We conclude this study by proposing an energy-transfer process involving ions randomly distributed throughout the glass media and acting as sinks and emitters through which the energy is spatially transferred.

The oxide glass matrix 40SiO$_2$·30Na$_2$CO$_3$·20PbO·10ZnO (mol %) used in this study was synthesized using SiO$_2$ as glass former, Na$_2$CO$_3$ to reduce the melting point, PbO to increase the refraction index, and ZnO as intermediate oxide. The host template was doped with Nd$_2$O$_3$, the concentration ranging from 0.1 to 1.9 wt % in steps of 0.2 wt %. The mixture was melted in a porcelain crucible at 1000 °C for 30 min. Then, the samples were cooled down to room temperature and later on annealed at 350 °C for 3 h in order to release thermal stress. Samples of about 2 mm thick were polished for the purpose of optical characterization.

A temperature-controlled cryostat, coupled to the microluminescence setup, was loaded with samples for low-temperature measurements. For the photoluminescence (PL) measurements the sample-emitted light was dispersed in a 0.5 m spectrometer, whereas the PL signal was synchro-
nously detected using a nitrogen-cooled germanium detector. The samples were excited by an Ar⁺-ion laser (514.5 nm line) using normal incidence through a tightly focused laser beam (spot diameter ~3 μm) of a microscope objective. Due to photon migration throughout the sample the luminescent region is much wider than the excitation spot. The PL emission was collected from the sample surface back to the microscope objective. In the microhole setup the magnified image is scanned by a pinhole attached to micromovers that collect the light into the monochromator slit and to the detection system. The optical absorption (OA) spectra were obtained using a Varian Cary 500 Scan spectrophotometer operating in the range of 175–3300 nm.

Figure 1 shows the PL and OA spectra of a typical Nd₃⁺:YAG-doped glass (1.9 wt. %). The OA spectrum shows transitions ⁴F₁₅/₂ → ⁴I₉/₂ and ⁴F₃/₂ → ⁴I₉/₂ at about 514 and 876 nm, respectively, the former line corresponding the excitation line from the Ar⁺-ion laser. The PL spectrum shows three broad emissions centered at 1330, 1060, and 880 nm, corresponding to ⁴F₃/₂ → ⁴I₁₁/₂, ⁴F₅/₂ → ⁴I₁₁/₂, and ⁴F₃/₂ → ⁴I₉/₂ transitions, respectively. Since absorption and emission occurs in the optical window of 800–950 nm, we have investigated the photon diffusion inside this window by setting the spectrometer at 880 nm. This wavelength falls within the range of interest for both optical amplifiers and optical-fiber communications.

The optical pumping takes electrons from the Nd³⁺ ground state (⁴I₁₅/₂) to a relatively large band (⁴K₃/₂+⁴G₃/₂+⁴G₅/₂). In a short time, on the order of few picoseconds, the electrons decay to a lower excited state (⁴F₃/₂) metastable. The time decay of the direct transition from the metastable level to the ground state is much longer (on the order of microseconds) and is detected at 880 nm. The luminescence region detected on the sample surface is much wider than the spot area excited by the laser beam. This behavior is regarded as a photon-assisted energy-transfer process in which the photon generated inside the laser spot migrates outwards and stimulates ions outside the laser-excited area to the excited states. Therefore, an energy-transfer process through photon absorption/emission may account for the large luminescent region described in Fig. 2.

We quantified the photon-transport problem in terms of a measurable macroscopic quantity, such as the local photon density (n) inside the sample. This is accomplished by formulating the problem through the diffusion equation. We may adopt the diffusion approximation as the starting point of our analysis. The incident light excites Nd³⁺ ions in a small area at the sample surface and the energy can migrate outwards from this illuminated area using neighbor Nd³⁺ sites. According to the standard diffusion theory, after a time equal to the intrinsic lifetime of the ion excited, the excitation energy will be distributed over the surface according to the following equation:

\[
L_{ed} \frac{1}{r} \frac{d}{dr} \left( r \frac{dn}{dr} \right) - n = -G_0 \Phi(r),
\]

where \(G_0\) is a constant related to the laser excitation intensity, \(L_{ed}\) = \(D/\mu_\mu\) is the effective diffusion length, \(D\) is the diffusion constant, and \(\mu_\mu\) is the absorption coefficient.

Within the transport theory approximation scattered light can be described through a diffusion mean free path (\(L_{ed}\)) that determines the average distance the photon travels throughout the system before it is quenched. Since the diffusion length is much larger than the spot diameter, we may use a delta function to describe the laser excitation spot, located at \(r=0\). Thus, the analytical solution of Eq. (1) reads

\[
n(r) = a K_0 \left( \frac{r}{L_{ed}} \right),
\]

where \(a\) is a constant and \(K_0(\mu/L_{ed})\) is the zero-order modified Bessel function. The observed luminescence intensity \((I_{pl})\) is proportional to the concentration of the excited ions. Since the density of emitted photon is proportional to the ion concentration, consequently the local photon density \(n\) can be read directly from the luminescence spatial profile curve as shown in Fig. 2. Thus, the photon migration inside the sample can be shown to follow the diffusion equation solution and Eq. (2) may be used to fit the slope of the luminescence spatial profile curves.
Figure 3 shows the values of $L_{\text{ef}} \times \text{wt } \%$ obtained from fitting the data shown in Fig. 2, using $L_{\text{ef}}$ as the fitting parameter in Eq. (2). From the analysis of the data shown in Fig. 3, we can determine the maximum value of $L_{\text{ef}}$ that provides the most efficient spatial energy transfer. The largest diffusion length, according to Fig. 3, is obtained at 1.1 wt % Nd$_3$O$_5$.

At low concentration values ($N<0.7 \text{ wt } \%$) the photon diffusion length may be limited by the distance between Nd$^{3+}$ ions, meaning that energy transfer decreases as the mean distance between ions increases. At low Nd$^{3+}$-ion concentration the absorption of photons is minimized and the probability to lose these photons by scattering is higher. Actually, the absorption coefficient is an increasing function of the Nd$^{3+}$-ion concentration. Nevertheless, as the Nd$^{3+}$-ion concentration increases ($0.7<N<1.3 \text{ wt } \%$) the diffusion length increases and saturates at approximately 1.1 wt %. This means that the diffusion constant ($D$) might increase as the Nd$^{3+}$-ion concentration increases. On the other hand, as the Nd$^{3+}$-ion concentration increases further ($N>1.3 \text{ wt } \%$) other possibilities of relaxation, such as nonradiative decay and cross relaxation, are more effective than the spatial energy transfer, also observed as a decay of lifetime ($\tau$) shown in the inset of Fig. 3. Possible excitation scattering mechanisms include defects, optical phonons, and acoustic phonons. Effects of surface quenching have been observed in other types of materials with high absorption coefficients such as Nd$_3$La$_{1-x}$O$_{14}$ crystals.

One possible explanation for the photon diffusion originates from the microscopic nature of the interaction of an ion-excited state undergoing a random walk due to electric dipole-dipole interaction. If we try to use the dipole-dipole interaction, using the values of $L_{\text{ef}}$ displayed in Fig. 2, it is easy to show that the estimated distance between ions would be in the range of 50–70 nm, which is quite large in comparison with the values established for the Förster mechanism. For this reason we should analyze the energy transfer in terms of both the absorption coefficient and the mean free path for photons. Therefore, the energy-transfer process is regarded as a long-mean-free-path random walk in which the migrating photons are scattered by defects or phonons.

In conclusion, we have used a simple approach to measure the photon diffusion length and the spatial energy transfer in Nd$^{3+}$-doped glasses. Since the largest diffusion length was observed for the 1.1 wt % Nd$_3$O$_5$ concentration, we argue that this is the best concentration for optical devices that need high-energy transfer such as optical amplifiers.

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Spatial energy transfer in Nd\(^{3+}\)-doped glasses as a function of concentration

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Available online 8 August 2006

Abstract

Energy transfer processes and the related photon diffusion in Nd\(^{3+}\)-doped glasses were investigated. A spatially resolved microluminescence technique was used to measure the spatial distribution of the emitted light as a function of Nd\(^{3+}\)-ion concentration. The most efficient concentration for long range photon diffusion was determined as a function of emitting wavelengths. Concentrations of 1.1 wt% Nd\(_2\)O\(_3\) at 880 nm, 1.2 wt% at 1060 nm, and 0.9 wt% at 1330 nm were found. An energy transfer process that involves ions randomly distributed throughout the glassy media at the same time acting as sinks and emitters of photons through which the energy is spatially transferred was proposed.

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Keywords: Laser–matter interactions; Optical properties; Absorption; Luminescence; Optical spectroscopy; Oxide glasses; Rare-earths in glasses

I. Introduction

Rare-earth ions play an important role in much of modern optical technology as the active constituents of materials. There are an amazing number of applications for these rare-earth-activated materials and much of today’s cutting-edge optical technology and future innovations rely on their unique properties [1–4]. In particular, the use of rare-earth ions emitting in the optical fiber spectral region has attracted considerable interest as a new field of luminescent materials [5,6].

Energy transfer mechanisms investigated by photon diffusion have attracted a lot of attention and have been studied in many material systems, such as polymers [7], dielectric crystals [8], semiconductor heterostructures [9], biological material [10], and other various media [11]. In order to probe the luminescence source distribution in a diffusive medium, it is usual to make use of diffusive light [12]. Within the transport theory, propagation of light in a material medium can be described through a mean-free-path that determines the average distance the photon travels throughout the system before it is quenched. The extent to which information can be extracted from this approach obviously depends upon the accuracy with which one can model the photon migration by means of multiple scattering. Thus, a complete characterization of the optical properties of a particular material is important not only for technological reasons but also for obtaining a better understanding of the energy transfer processes involved [9,13].

In this paper, an experimental investigation of Nd\(^{3+}\)-doped glasses was carried out to evaluate the photon migration mechanisms and the strength of the coupling between Nd\(^{3+}\)-ions by analyzing the spatially resolved
microluminescence (ML) on the sample surface. In order to perform this study, Nd$_2$O$_3$-doped oxide glasses were synthesized with a Nd$_2$O$_3$ concentration (N) ranging from 0.1 to 1.9 wt%. The photon effective diffusion length ($L_{ef}$) as a function of Nd$_2$O$_3$ concentration was obtained.

2. Sample preparation and experimental details

The SNPZ oxide glass matrix: 40SiO$_2$: 30Na$_2$CO$_3$: 20PbO: 10ZnO (mol%) used in this study was synthesized using SiO$_2$ as the glass former, Na$_2$CO$_3$ to reduce the melting point, PbO to increase the refractive index, and ZnO as intermediate oxide. The host template was doped with Nd$_2$O$_3$, in concentrations ranging from 0.1 to 1.9 wt% in steps of 0.2 wt%. The mixture was melted in a porcelain crucible at 1000°C for 30 min. Then, the samples were cooled down to room temperature and later annealed at 350°C for 3 h in order to release thermal stress. The samples were polished to about 2 mm thick for optical characterization purposes.

A variable temperature cryostat, coupled to the microluminescence setup, was loaded with samples for low-temperature measurements. For the photoluminescence (PL) measurements, the samples were excited by a CW Ar$^+$ ion laser, and the emitted light from the sample surface was dispersed by a 0.5 m spectrometer, whereas the PL signal was synchronously detected by a nitrogen-cooled germanium detector. The optical absorption (OA) spectra were obtained using a Varian Cary 500 scan spectrophotometer operating in the range of 175–3300 nm.

For microluminescence (ML) measurements, a CW excitation laser beam from an Ar$^+$ ion laser was tightly focused onto a microsized spot (spot diameter $\sim$3 μm) on the sample surface. The incident laser beam hit the surface at normal incidence and excited electrons in the illuminated area to the higher order energy levels of the Nd$^{3+}$ ions. After the characteristic lifetimes were over, the electrons return to the low-energy excited states by emitting photons. Photons migrate outwards from the laser spot region, thus creating a wide luminescent area around the spot. The light from this luminescent area is collected through the same microscope objective and redirected to the detector system. A beam-splitter prism was used to reflect the light coming back from the sample towards the scanning device, including both the reflected excitation laser and the sample luminescence. The laser line went along with the luminescent lines until an optical filter blocked it. The scanning device consisted of a pinhole, a microscope objective, and a mirror attached to micro-translators stages driven by step motors. The projected image of the luminescent area was one order of magnitude magnified at the focal plane. Thus, the scanning device was able to move across the diameter of the projected image. The synchronous lock-in detection technique and a liquid-nitrogen-cooled Ge detector were used to measure the luminescence intensity. The magnified image was scanned by the pinhole attached to micro-translators that collect the light into the monochromator slit and to the detection system [8]. The luminescence intensity was measured and recorded as a function of the radial distance of the pinhole to the excitation laser spot.

3. Experimental results

Fig. 1 shows the PL and OA spectra of a typical Nd$^{3+}$-doped glass (1.9% wt Nd$_2$O$_3$). The OA spectrum shows the following transition $^4$I$_{9/2}$ $\rightarrow$ $^4$F$_{3/2}$ that matches exactly the 514 nm pumping line from the excitation Ar$^+$ ion laser [14]. The excited states of the PL spectrum show three broad emissions centred at 1330, 1060, and 880 nm, which correspond to $^4$F$_{3/2}$ $\rightarrow$ $^4$I$_{13/2}$, $^4$F$_{3/2}$ $\rightarrow$ $^4$I$_{11/2}$, and $^4$F$_{3/2}$ $\rightarrow$ $^4$I$_{15/2}$ transitions, respectively. In fact, in the measurements, the photon diffusion was investigated by setting the spectrometer to these specific wavelengths, which fall within the range of interest for both optical amplifiers and optical fiber communications.

The CW optical pumping took electrons from the Nd$^{3+}$ ground state ($^4$I$_{9/2}$) to a relatively large band ($^4$K$_{13/2}$ + $^2$G$_{7/2}$ + $^2$G$_{9/2}$). In a short time, in the order of a few picoseconds [15], electrons decayed to a lower excited state ($^4$F$_{3/2}$ metastable). The decay time of the direct transition from the metastable level to the ground state was much longer (in the order of microseconds) and was detected at 880 nm. According to the absorption and emission spectra, the following transitions $^4$I$_{9/2}$ $\rightarrow$ $^4$F$_{3/2}$ and $^4$F$_{3/2}$ $\rightarrow$ $^4$I$_{15/2}$ overlapped at around 880 nm, which is an interesting behaviour as it could be used for optical fiber amplifiers.

In Figs. 2, 4 and 6 the spatially resolved microluminescence images have been plotted. The luminescent region detected on the sample surface was much wider than the spot area ($\sim$7 μm$^2$) excited by the laser beam. This is exactly the behaviour which is regarded as a photon-assisted energy transfer process, in which the photon generated inside the laser spot migrates outwards and stimulates

![Image](image-url)

**Fig. 1.** Optical absorption (dotted line) and photoluminescence (solid line) spectra of 1.9 wt% Nd$_2$O$_3$-doped glass.
ions outside the laser excited area to excited states. Therefore, an energy transfer process through photon absorption/emission would account for the large luminescent region described.

4. Discussion

In order to study the phenomenon observed in Figs. 2, 4, and 6, the photon transport problem in terms of a measurable macroscopic quantity, such as the local photon density \( n \) inside the sample, has been quantified. This was accomplished by formulating the problem through the diffusion equation \([8,9,11,12]\). The incident light excites \( \text{Nd}^{3+} \)-ions in a small area on the sample surface and the energy diffuses outwards from this illuminated area using neighboring \( \text{Nd}^{3+} \) sites. According to the standard diffusion theory, after a period equal to the intrinsic lifetime of the ion-excited state, the excitation energy will be distributed over the surface according to the following equation:

\[
\frac{d}{dt} \frac{1}{r} \frac{dn}{dr} - n = -G_{0} \delta(r),
\]

where \( G_{0} \) is a constant related to the laser excitation intensity, \( L_{\text{eff}} = \sqrt{D/\mu_{a}} \) is the effective diffusion length, \( D \) is the diffusion constant, and \( \mu_{a} \) is the absorption coefficient.

Within the transport theory approximation, the scattered light can be described through a diffusion mean-free-path \( (L_{\text{eff}}) \) that determines the average distance the photon travels throughout the system before it is quenched. Since the diffusion length is much larger than the spot diameter, we may use a delta function to describe the laser excitation spot, located at \( r = 0 \). Thus, the analytical solution of Eq. (1) is given by the zero-order modified Bessel function, \( K_{0}(r/L_{\text{eff}}) \):

\[
n(r) = aK_{0} \left( \frac{r}{L_{\text{eff}}} \right),
\]

where \( a \) is a constant. The observed luminescence intensity \( I_{PL} \) is proportional to the concentration of excited ions. Since photon density is proportional to the ion concentration, consequently the local photon density \( n \) can be read directly from the microluminescence spatial profile, as shown in Fig. 2. Thus, inside the sample, the photon diffusion would follow the diffusion equation solution, and Eq. (2) may be used to fit the slope of the ML spatial profiles.

Initially, the diffusion lengths \( (L_{\text{eff}}) \) are obtained by fitting the ML profiles of Fig. 2 by using Eq. (2). Fig. 3 shows the values of \( L_{\text{eff}} \) as a function of the corresponding \( \text{Nd}^{3+} \)-ion concentration (wt%). From the analysis of this curve, the top value of \( L_{\text{eff}} \) that theoretically would provide the most efficient spatial energy transfer inside the glassy system can be determined.

At 880 nm, the highest \( L_{\text{eff}} \) according to Fig. 3 was found at 1.10 wt% \( \text{Nd}_{2}O_{3} \). This was the first result; exactly
the same measurements were carried out for the other transitions, i.e., at 1060 nm and 1330 nm, in order to check whether the photon would demonstrate similar behaviour as a function of Nd³⁺ concentration. The ML profiles have been plotted in Figs. 4 and 6. In addition, the dependence of $L_{\text{eff}}$ as a function of the Nd³⁺-ion concentration has been plotted in Figs. 5 and 7. Thus, from Fig. 5, the highest $L_{\text{eff}}$ was found at 1.2 (%wt Nd₂O₃), detected at 1330 nm. From Fig. 7, the highest $L_{\text{eff}}$ was found at 0.9 (% wt Nd₂O₃), detected at 1330 nm.

The photon diffusion lengths as a function of their energies at the specific concentration of 1.1% wt Nd₂O₃ have been plotted in Fig. 8, demonstrating that the diffusion length increases as the emission energy decreases.

One possible explanation for the photon diffusion inside the glassy media originates from the microscopic nature of the interaction of an ion-excited state undergoing a random walk due to electric dipole-dipole interaction. Using the dipole-dipole interaction [16,17], with the values of $L_{\text{eff}}$ displayed in Fig. 2, it is easy to show that the estimated distance between ions would be in the range of 50-70 nm, which is quite large in comparison with the values established by the Förster mechanism [16,17]. This is one of the reasons for analyzing the energy transfer in terms of multiple absorptions and emissions that on average represents the mean-free-path for photons.

In this paper, the best Nd³⁺-ion concentration for enhancing energy transfer inside the sample was determined. However, to understand what is behind the energy transfer mechanisms physically, the curve of Fig. 3, for instance, will be taken, and the photon diffusion coefficients at different concentration ranges analyzed. At low concentration values ($N < 0.7$ wt% Nd₂O₃), photon diffusion may
be limited by the distance between neighbouring Nd\(^{3+}\) ions, meaning that energy transfer decreases as the mean distance between ions increases. At low Nd\(^{3+}\)-ion concentration, the absorption of photons is minimized and the probability of losing these photons by scattering is higher. Actually, the absorption coefficient is an increasing function of the Nd\(^{3+}\)-ion concentration. Nevertheless, as the Nd\(^{3+}\)-ion concentration increases (0.7 < N < 1.3 wt% Nd\(_2\)O\(_3\)) the diffusion length increases and saturates at approximately 1.1 wt% Nd\(_2\)O\(_3\). This means that the diffusion constant (D) may increase as the Nd\(^{3+}\)-ion concentration increases. On the other hand, as the Nd\(^{3+}\)-ion concentration increases further (N > 1.3 wt% Nd\(_2\)O\(_3\)) other possibilities of relaxation, such as non-radiative decay and cross relaxation, become more effective than the spatial energy transfer. Possible excitation scattering mechanisms include defects, optical phonons, and acoustic phonons.

5. Conclusion

In conclusion, a spatially resolved microluminescence technique was used to measure the spatial distribution of emitted light in Nd\(^{3+}\)-doped glasses, as a function of doping ion concentration. Different concentrations for specific wavelengths were obtained. Thus, different wavelengths would have different best concentration. The spatial distribution of the luminescence was studied and the energy transfer processes among Nd\(^{3+}\)-ions were discussed. The most efficient concentrations of Nd\(^{3+}\)-ions embedded into the glassy matrix that give higher energy transfer were found. Efficient long-range photon migration was determined for specific emitting wavelengths: 1.1 wt% Nd\(_2\)O\(_3\) at 880 nm, 1.2% wt at 1060 nm, and 0.9% wt at 1330 nm. The overall view of the observed behaviour was that an energy transfer process was proposed, where ions randomly distributed throughout the glass media acted as sinks and emitters through which the energy is spatially transferred.

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References

Optical properties of IV–VI quantum dots embedded in glass: Size-effects

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Abstract

Measurements of the photoluminescence (PL), micro-PL, spatially-resolved PL, optical absorption and atomic force microscopy (AFM) of PbS and PbSe quantum dots (QDs) embedded in oxide glass matrix, were carried out. It was found that the energy gaps of the QDs showed pronounced anomalous temperature dependences. Their temperature coefficients depended strongly upon the size and shape of the QDs, and surface and/or confined phonon modes. In addition, the energy-dependent transfer rate of excitons from smaller to larger dots via electronic coupling was observed. It was predicted that further improvements in size selectivity, luminescence quantum yield, and well-controlled growth would enable highly efficient inter-dot energy transfer.

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Keywords: Nanocrystals; Glasses; Optical spectroscopy; Atomic force and scanning tunneling microscopy; Quantum wells, wires and dots; Absorption; Luminescence

1. Introduction

In the last few years, semiconductor quantum dot (QD)-doped glasses that behave as artificial atoms with discrete, size-tunable electronic transitions, have attracted a great deal of attention, particularly due to application in the 1.3–1.55 μm range of optical communications [1–4]. IV–VI semiconductor QDs, such as PbS and PbSe QDs, provide unique access to the limit of strong quantum confinement and are excellent for investigation of the properties of a size-quantized system. In contrast to II–VI and III–V materials, both the electron and hole are individually strongly confined in lead-salt QDs. The exciton Bohr radius of dBoh = 46 nm in PbSe is eight times larger than in CdSe [1]. The dominant features of the electronic structure are reasonably well established: the continuum states of the bulk semiconductor transforming to the discrete states of the QD and the shift of the interband transitions with QD size have been thoroughly studied [5,7]. However, the effects of quantum confinement on the temperature dependence of the energy gap of a semiconductor IV–VI quantum dot are not well established for QDs [6]. In addition, in strongly coupled quantum dot assemblies, electronic excitations can, in principle, delocalize across multiple dots leading to new states described by coherent superposition of individual dot wave functions that are not well understood. In this paper, a study of the temperature dependence of the energy gap of IV–VI QDs and the evaluation of the coupling strength between PbX QDs by analyzing the spatially-resolved photoluminescence are reported.

2. Experimental details

The sulphur (selenium)-doped oxide glass matrix (SiO2–Na2CO3–Al2O3–PbO2–B2O3) used in this study was
prepared from high purity powders using SiO₂ as the glass former. The dopant concentration was 2-weight percentage of glass matrix. The mixture was melted in an alumina crucible at 1200 °C for 30 min. Then, it was cooled down to room temperature. After that, a thermal treatment of the glass matrix was performed at 500 °C to enhance the diffusion of Pb²⁺ and S²⁻ (Se²⁻) ions. The corresponding annealing times of the two S-doped glasses were 3 and 5 h, while for the two Se-doped glasses, they were 5 and 12 h. Finally, PbS (PbSe) QDs were created in the glass matrices. For the PL measurements, the emitted light was dispersed by a 0.5 m spectrometer, and the PL signal was synchronously detected by a nitrogen-cooled germanium detector. The samples were excited by an Ar-ion laser using the 514 nm line (excitation energy of 2.34 eV) with normal incident light through the tightly focused laser beam (spot diameter 5 μm) of a microscope objective. Due to energy transfer, the luminescent region became larger than the excitation spot. The PL emission was collected from the back of the sample surface into the microscope objective. The magnified image was scanned through a pinhole that let light into the monochromator. In order to measure the energy transfer among nanocrystals, spatially-resolved microluminescence was performed [12].

3. Results

Fig. 1 shows the AFM image (2 μm × 2 μm) of the PbS-doped glass matrix annealed for 3 h. The inset illustrates the morphology of a PbS quantum dot. Clear images of PbS QDs can be seen. The shape of the individual QD looks spherical, although a small deviation is observed. The average diameter of the QD is 4.2 nm, with a QD-size dispersion of about 6%.

Fig. 2 shows the thermal treatment controlled emission (dotted lines) and optical absorption (solid lines) spectra of PbS (a) and PbSe (b) quantum dots at room temperature. It is found that for both PbS- and PbSe-doped glasses, emission maximum shifts to longer wavelengths with increased annealing time. Comparison between the data obtained from numerical k·p calculations of the energy levels [10,11] and the energy observed in the optical absorption spectra can be used to estimate the PbS QD sizes. Through this method, the estimated average diameter of the QDs in the PbS-doped glasses annealed for 3 and 5 h, was 4.4 and 5.1 nm, respectively. They were consistent with the AFM observations in terms of average diameter [3]. It was also noted that the annealing process changed the Stokes shift. For the PbS- and PbSe-doped glasses annealed for 5 h, the Stokes shifts were 137 and 48 meV, corresponding to 12% and 3% of their recombination energies, respectively.

Fig. 3 illustrates the evolution of the PL spectra as a function of temperature for the PbS sample annealed for 3 h (a) and PbSe annealed for 12 h (b). It is noted that both
samples presented similar band gap temperature dependence, but with different $dE_g/dT$ rates. A detailed calculation of the average value of $dE_g/dT$ was performed through Fig. 3 for both samples. They were given as 113 $\mu$eV/K for the PbS QD and 70 $\mu$eV/K for the PbS QD, respectively. They are quite different to the value of $dE_g/dT$ in the bulk material (500 $\mu$eV/K).

Fig. 4 displays the PL spatial distribution of the PbS-doped glass annealed for 3 h measured at different emission energies. The inset shows the PL spectrum. The detection energies used to probe the PL spatial profile are indicated by the vertical arrows. It was observed that the detection energy strongly influenced the energy transfer process. The lower the detection energy, the larger the diffusion length. This behavior results from the energy transfer between different subsets of QDs. In fact, larger detection energies can be used to create electron-hole pairs in smaller quantum dots. As mentioned previously, the lights with high energy emitted by the recombination of these electron-hole pairs may excite various QDs with larger sizes. Because of the dispersion of QD-size, the probability of absorption of incident light is very large. In contrast, in the case of lower detection energies, the incident light can only create the electron-hole pairs in larger QDs. The photons emitted by these QDs can only be absorbed by even larger QDs. Statistically, the probability of absorption of these photons is much lower than that in the higher detection energy case. Hence, a wider PL spatial distribution would be expected.

Fig. 5 shows the results of similar measurements to those carried out in Fig. 4, except that the sample under consideration is the PbSe QD-based material. It is noted that the PbSe QDs presented a similar behavior to PbS QDs. This provides more strong support for the mechanism of the energy flow process among different subset of dots.

Fig. 6 displays the PL spatial profiles of the PbS samples annealed for 3 h (solid line) and 5 h (dashed line), obtained by detecting the signal at the PL peak position related to

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**Fig. 3.** PL spectra of PbS (a) and PbSe (b) quantum dots as a function of temperature.

**Fig. 4.** PL spatial profile of the PbS quantum dots measured at different detection energies. The inset shows the PL spectrum, in which the vertical arrows indicate the detection energies used in the PL spatial profile measurement.

**Fig. 5.** PL spatial profile of the PbSe QDs measured at different detection energies. The inset shows the PL spectrum, in which the vertical arrows indicate the detection energies used in the PL spatial profile measurement.
each QD sample, at $T = 290\, \text{K}$. Since the luminescence on the sample surface is symmetrical around the laser excitation spot, only the PL intensity profile starting from the centre of the spot (centred at 0 µm) was plotted. It was found that the sample annealed for 3 h presented a longer diffusion length than that of the sample annealed for 5 h. The underlying physics of this annealing time dependent PL spatial profile is that during the thermal process, the individual QDs were first created. Then the nearest neighboring QDs tended to glue together to form new QD with a larger size. For the sample created by the thermal treatment with a short annealing time, two individual nanocrystal QDs inside the sample only have a very low probability of gluing together and forming the new different sized QD [14]. Hence the variation of QD size is relatively small. Consequently, the emission-reabsorption process that occurs between two different sized QDs is largely blocked. Therefore, the photons can diffuse a long distance before they are absorbed. In contrast, for the sample created by thermal treatment with a long annealing time, two individual nanocrystal QDs have enough time to glue together to create the new different sized QD. Then, a large dispersion of QD sizes is expected. Hence, the emission-reabsorption process will be strongly enhanced, shortening the photon diffusion length.

4. Discussion

Dependence of the transition energy on the QD size allows the 'tuning' of the glasses to a wavelength of a specific light source if the energy of photons at a desirable wavelength exceeds the energy gap of the bulk semiconductor, and resonance 'tuning' is possible if the QDs $dE_d/dT$ are narrowly size distributed [8,9].

The band gap of bulk IV–VI semiconductor materials present a positive temperature dependence $dE_d/dT$ coefficient; i.e., the band gap increases as the temperature increases [6]. Three-dimensional confinement of electrons to a nanometer-sized space makes their continuous energy spectrum more discrete. It not only modifies electronic state, but also modifies phonon spectrum to size-dependent discrete lines. Hence the electron-confined phonon and exciton–confined phonon interactions are also thought to be changed. In addition, the effects of QD size also contribute to the variation of electron–surface phonon and exciton–surface phonon interactions. Therefore, it is expected that the temperature dependence of the band gap changes with the variation of the QD size.

The photon diffusion length ($L$), which measures a photon-assisted energy transfer process in which the photons generated inside the laser spot migrate outwards stimulating the surrounding dots, is the average distance that the photon travels in the material before it dissipates. It is used to characterize nanocrystal samples that contain different assemblies of QD sizes. Recently, spatially-resolved PL (SRPL) has been used to investigate photon diffusion length and the strength of interaction among dots [12]. Because QDs have discrete, size-tunable electronic transitions, an energy transfer may take place between two quantum dots with different sizes [13–15]. The subset of small dots emits a high energy light. In addition, the strong confinement increases the overlap between electron and hole wave function, enhancing the intensity of the QD laser made up of small QDs. Then, the small QDs may be used as a light source to excite the subset of larger dots. If the distance between two QDs of different size is smaller than the photon diffusion length, the photons that are emitted from the small dots can be absorbed by the large-sized dots.

5. Conclusion

The structural and optical characterization of PbS- and PbSe-doped glasses were presented. The controlled synthesis of IV–VI quantum dots with narrow size distributions was achieved through controlling the annealing process, annealing temperature and time. When the annealing time is prolonged, the peak position of the OA spectrum moves to the lower energy side, indicating an increase in QD size. When the temperature increases, the recombination energy presents a large blue shift. The degree of the energy shift can be tuned by the annealing process. The calculated energies of the optically allowed exciton states through the $4 \times 4$ $k \cdot p$ theory were found to be in good agreement with experimental data [2]. Energy transfer processes in nanocrystals immersed in glass templates were also investigated. The measurements clearly revealed the energy transfer from smaller to larger dots. Energy transfer between dots with different sizes is quite reduced when reabsorption is significantly high. Based on these findings, it is predicted that further improvements in size selectivity will permit highly efficient energy flows between quantum dots.
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References

Electric field effect in the spin dynamics of self-assembled InAs/GaAs quantum dots

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Abstract

We identify fundamental mechanisms of electron and hole dynamics in self-organized InAs/GaAs quantum dots (QDs) subject to vertical electric fields by photocurrent investigations. We propose a spin-flip mechanism involving a spin exchange between neighboring QDs. The spin-flip process is revealed in the photocurrent dynamics when the exciton population increases unexpectedly with reverse bias.

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Keywords: Quantum dot; Spin; Electric field; Photocurrent

1. Introduction

Self-assembled quantum dot (QD) structures are potentially promising for memories due to the large confinement energy for holes. The spin of an electron or a hole in such structures is very important in determining their electronic and optical properties. Its manipulation has great potential in spintronics and quantum information processing [1–3]. One of the most intensively studied self-assembled QD systems is the InAs/GaAs system. Experimental evidence of a dynamical process of dots charging and discharging with photogenerated holes and electrons revealed by the photocurrent measurements under illumination is presented and discussed.

Experimental results allow us to verify the influence of an electric field and of charging effects on excitons optically excited in a self-assembled QD. Photocurrent spectroscopy is a suitable technique to investigate the absorption of a QD, which can give information on the mechanisms of capture and escape [4]. Tunneling carrier escape has been detected and confirmed in InAs QDs [5–7].

We report here a novel process that offers control over the conversion of dark into bright excitons in a QD. An electron spin is exchanged with a spin in an adjacent QD by a coherent Kondo-like tunneling interaction. Dark excitons have shown long lifetimes, which are attractive for applications, but it is still a challenge to manipulate dark excitons in a controlled way. It is pointed out that a spin-flip mechanism can occur in a controlled fashion in self-assembled QDs, and we present a qualitative model that explains the observed behavior through photocurrent results.

2. Experiment

The sample studied was a GaAs p–n–n diode structure grown by molecular-beam epitaxy at 500 °C with five layers of InAs dots separated by 20 nm of undoped GaAs. The dots were formed from 2.4 ML of InAs deposited at 0.39 ML/s using Stranski–Krstanow technique, and had a density of about 5 × 10^10 cm^-2. The electric field F across the intrinsic region is controlled by the built-in potential...
(U_0) and the applied bias (U). Mesas with 400 µm were employed.

The samples were mounted in a variable temperature cryostat coupled with the measurement system. The samples are excited with energy of 1.94 eV by a HeNe laser. For this energy, the electron–hole pairs are excited into higher QD levels. For the PL measurements, the emitted light was dispersed by a 0.8 m spectrometer and detected by a liquid-nitrogen-cooled Ge detector using standard lock-in technique. For the photocurrent measurements, a micro-PL set-up was used to excite the mesas. Since only the QDs in the contact region significantly contribute to the PC signal, it was possible to chop the laser beam and to measure the modulated signal with a lock-in amplifier.

3. Experimental results and discussions

At low temperatures, escape from the dots occurs by tunneling. By varying the electric field we control the tunneling rate and we are able to observe its competition with relaxation and recombination. Fig. 1a shows the PL spectrum of the corresponding InAs/GaAs QD structure. In Fig. 1b and c, the variations of the intensities of the PL and PC are plotted against applied voltage (U) at low temperature (T = 10 K). The PC intensity shows the inverse dependence compared to the PL, providing evidence for competition between tunneling and radiative recombination. Thermal escape out of the QD is negligible with respect to the tunneling escape due to the low temperature [8].

Fig. 1b displays the field dependence of the PL intensity at different detection energies (1–4). It was obtained using excitation at 1.94 eV from a HeNe laser. Both PL × U and PC × U show a pronounced shoulder at U = −1.177 V. The shoulder is significantly more pronounced when detected on the low-energy side of the QD emission, i.e., on large dots. In fact, this behavior will be associated with the spin–flip mechanism. The value of the reverse bias with the onset of saturation of the PC signal coincides with the value of the bias where the shoulder is observed on the PL intensity. PC is complementary to PL since it detects those excitons that are excited in the dots and then escape by tunneling. So, a very good anticorrelation between the two processes is observed in Fig. 1, showing that tunnel escape dominates the PL quenching.

By adjusting the bias applied between the n and p contact layers, we control the electron occupation of the dots. In a p–n diode, the tunneling times for electrons and holes are obtained considering \( F = F_0 + \Delta F \), where \( F_0 = (U_n - U) / d \) and \( \Delta F = (n_e - n_h) e N_{QD} / \epsilon_0 \). The electric field across the intrinsic region is controlled by the built-in potential \( (U_n - U) = 1.5 V \) and the applied bias (U) and d is the width of the intrinsic region. At low electric fields, the holes as well as the electrons stay in the QD and recombine. Charge accumulation caused by tunneling of optical carriers can be excluded. At high reverse bias, the internal electric field is strong enough to separate the optically excited excitons. The electrons as well as the holes tunnel out of the QDs at different rates. In a previous work, the reverse bias is increased between −2 and −6 V, the photocurrent behavior demonstrates that carriers can only tunnel out from the dots for \( U < -2 \) V; for \( U > -2 \) V, they relax to the ground state and recombine [4].

Fig. 2 shows the PL intensity as a function of energy for different applied voltages. It is clear that the strongest change with voltage occurs at high energies, which demonstrates the dependence of carrier tunneling on the QD emission energy. Tunneling escape produces changes in the PL intensity due to the promotion of photoexcited excitons towards smaller or bigger dots around the average size distribution. The probability of tunneling and escape
of electrons out of the dots is higher in the small dot subset due to the more shallow nature of the confined electrons level as compared to the situation of the large dots. The consequence of this is the quenching of the PL intensity at $E_{\text{ex}} \approx 1.27$ eV, since electrons are dominated by tunneling out of the dots. On the other side, the PL intensity at $E_{\text{ex}} \approx 1.17$ eV depends on the radiative recombination of electrons and holes into bigger dots and are less affected by the tunneling process.

In a self-assembled QD, in addition to the two bright excitons with angular momentum $L_z = +1, -1$, there are two dark excitons with $L_z = +2, -2$ that do not couple to the light field [3]. The dark excitons are located few hundreds of μeV below the bright excitons and are also much longer lived than the bright excitons. Fast relaxation processes dominate such that the dark and bright excitons ($X^0$) are created with equal probabilities. Direct recombination of the dark exciton is disregarded, as both laser spectroscopy and cw PL on these dots have not revealed any admixture of the dark states with the bright states [9].

Dark and bright excitons exhibit different tunneling lifetimes. The tunneling time for the dark excitons out of the dots are expected to be much larger [3]. This large lifetime enables to accumulate dark excitons given that, in the steady state, the generation rate of dark excitons is equal to the tunneling rate. In steady state, there is a high probability of an electron tunneling from a small dot to a large dot in the vicinity, assuming that small dots have small confining potential. In this theory, small size dots work as a reservoir for spin tunneling. This transition is schematically shown in Fig. 3. The dark excitons contribute to the PL signal by undergoing a spin–flip, becoming bright and decaying radiatively. The spin–flip mechanism accounts for the spin exchange with neighbor QDs. Based on these arguments, we suggest that the increase in the PL intensity at $U = -1.177$ V is determined by both exciton spin–flip and radiative decay. The interactions between two spins, as well as those for two excitons, result from carrier tunneling between different dots and Coulomb interactions [10].

We propose that the interaction arises through an electron spin–flip involving small QDs as spin reservoir, as shown in Fig. 3, with the hole spin remaining unchanged. In terms of an interaction via virtual states $|\psi\rangle$, the electron in the dark exciton tunnels to an empty state of a neighbor QD, leaving the dot in the hole-only state. Then, an electron with opposite spin tunnels into the dot from a filled state creating a bright exciton.

4. Conclusion

We report on the carrier dynamics in InAs/GaAs self-assembled QDs. With photocurrent spectroscopy we have investigated the optically excited electron–hole pairs in the QDs under different electric fields and charging conditions. The results reveal a spin–flip process in the photocurrent dynamics when the exciton population increases unexpectedly with reverse bias.

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References


Anomalous photocurrent in self-assembled InAs/GaAs quantum dots

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Carrier dynamics in self-assembled InAs/GaAs quantum dots (QDs) is studied by photoluminescence (PL) and its complementary photocurrent (PC) spectroscopy. We found that carrier capture from the GaAs barriers, radiative recombination in InAs quantum dots, and tunneling among vertical QDs are very sensitive to applied bias voltage. An unusual behavior, by which the PL intensity presents step-like bias voltage dependence, has been observed. It is also consistently manifested in bias voltage dependent PC signals. We attribute this anomalous behavior to the interplay between the coupling of lateral QDs and tunneling among vertical ones. © 2008 American Institute of Physics. [DOI: 10.1063/1.2920763]

InAs/GaAs self-assembled quantum dots (QDs) have attracted widespread interest due to both their atomic and molecularlike electronic structures. They are also promising for ultralow threshold lasers, memories, spintronics devices, and quantum information processing. Photoluminescence (PL) and complementary photocurrent (PC) spectroscopies, both as a function of electric field, had been used to probe carrier capture and escape mechanisms in single InAs/GaAs QDs by Fry et al. They reported that PL intensity monotonically decreases with increasing bias voltage due to the competition between tunneling and radiative recombination. Knowledge of atomlike states in single QDs naturally leads to interest in molecular states of coupled QDs, or artificial molecules, because they can be formed by coupling the atomlike states in two dots. Moreover, several additional quantum physical processes, which may be used to create novel functionalities of QD-molecule devices, emerge. Among them, the quantum dot molecule states and single electron tunneling (SET) are intensively utilized in spintronics devices and quantum information processes. This motivated us to study the carrier dynamics in coupled QDs. In this letter, we report unusual step-like behavior of PL and PC signals observed in a sample consisting of five layers of InAs dots. A physical model to explain this anomalous behavior is also presented.

The sample studied is a GaAs p-i-n diode structure grown by molecular-beam epitaxy at 300°C with five layers of InAs dots well separated by 20 nm of undoped GaAs. The dots were formed from 2.4 ML of InAs deposited at 0.39 ML/s by using Stranski–Krastanow technique, and had a density of about \(5 \times 10^{10} \text{ cm}^{-2}\). The electric field \(F\) across the intrinsic region is controlled by the built-in potential \(V_B\) and the applied bias \(V_D\). The electric field \(F\) has been determined using the quantum dot molecule states and single electron tunneling (SET) are intensively utilized in spintronics devices and quantum information processes. This motivated us to study the carrier dynamics in coupled QDs. In this letter, we report unusual step-like behavior of PL and PC signals observed in a sample consisting of five layers of InAs dots. A physical model to explain this anomalous behavior is also presented.

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FIG. 1. (Color online) (a) PL spectrum of InAs/GaAs self-assembled quantum dots. (b) PL intensity vs applied voltage \(V_B\) at four different detection energies indicated by the corresponding letters in the PL spectrum. The insert shows the magnified picture of the shoulder in the PL intensity curves.

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larger the transition energy becomes. Thus, the PL signals marked by a, b, c and d are the emissions from four different QDs (dots a, b, c and d), whose size decreases from dot a to dot d. In order to study the dependence of PL and PC signals on QD size, we have performed our measurement at four different detection energies. The corresponding data are displayed in Figs. 1(b) and 2, respectively. It is noted that for Vg varies from 0.5 to ~0.5 V, the PL intensities show a very slight variation. While in the range from ~0.5 to ~1.0 V, the curves steeply change. Further increasing the reverse bias voltage, however, it presents an anomalous increase. After that, the PL intensity decreases once more. When the reverse bias voltage is larger than 2.0 V, the PL spectrum is completely quenched. Besides, this unusual step-like behavior shows strong detection-energy-dependence, e.g., it is significantly pronounced when PL is detected on the low-energy side of the emission spectrum. It is also worth noting that the PC intensity (Fig. 2) shows inverse bias voltage dependence with respect to the correspondent PL.

In the PC and PL measurements, the electron-hole pair is firstly created in the GaAs barrier region of the upper active layer. Then, they may be captured by their nearby QDs. After that, they relax from higher energy levels to the ground state of the correspondent QD, where the exciton is formed. Since the QDs are closely distributed in active layers, two adjacent QDs denominated by double lateral QDs are coupled, as shown in the upper part of Fig. 3. For two identical QDs, the coupling leads to the ground (bounding) and the first excited (antibounding) molecule states, which are completely delocalized over the entire double dot system, as shown in Fig. 3(a). Let us denote the ground and first excited states by E1 and E2. For two distinct QDs [Figs. 3(b) and 3(c)], both eigenstates E1(1) and E2(1) will be a mixture of symmetric and antisymmetric states, which are delocalized over both QDs as the previous case, but with a different probability. The energy difference ΔE between E1(1) and E2(1) is determined by ΔE = (ΔE0 + (2λ21)2, where ΔE0 represents the difference of the ground state energies of two isolated QDs, and λ21 denotes tunneling strength between them. Note that for a small ΔE0, the effect of the coupling is stronger. Whereas, for a large ΔE0, the E1(1) and E2(1) approach the energies of the unperturbed dots. Besides this xy-plane motion, the photo-created carriers are also driven by applied bias voltage to tunnel along growth (-z) direction. Hence, the single-particle Hamiltonian is described by $H = (\frac{\hbar^2}{2m} + V(x,y)) + (\frac{\hbar^2}{2m} + V(z))$, where $m$, $V(x,y)$, and $V(z)$ denote the effective electron mass, the confinement potential energy in xy-plane, and along z-direction, respectively. The electronic spectrum of the system will then be the summation over $E_1$ and $E_2$, where $E_1$ and $E_2$ denote the eigenvalues of the first (H1) and the second term (H2) of H. To understand the underlying physics of the PL and PC, we adopted a simple model in which we separate the motion in the growth and radial directions. For the former, we deal with double identical quantum wells, located in the nearest neighbor active layers, as shown in Fig. 3. Because of the large thickness of the barrier region between two active layers, we can safely neglect the quantum coupling between these two wells. Hence, the energy of the ground (E1(1)) and the first excited (E2(2)) states of H1 is equal to the corresponding ground state energy of each isolated well. For the radial direction motion, the energy spectrum of the system is supposed to be determined by a single lateral QD molecule. Based on this assumption, the lowest four energy levels of the system, denoted by E1(1), E2(1), E2(1), and E2(2), will then be given by E1(1) + E2(1), E1(1) + E2(2), E2(1) + E1(1), and E2(1) + E2(2), respectively. Since the electric field and the quantum Stark effect induce a shift of both E1(1) and E2(2) in reference to electrochemical potential of the emitter, but with different velocities, e.g., $E_2 < E_2$ for $V_g < 0$, a crossing of the states $E_2(1)$ and $E_2(2)$ occurs for a certain bias. Therefore, by tuning the bias voltage, we can make the system come into resonance. For zero bias, all discrete levels lie above the chemical potential of the emitter. Then, the current is basically zero. In the regime of low bias voltages, both the holes and the electrons are mainly confined in the QDs embedded in the upper active layer where they were generated. Because of the large overlap between the electron and hole wave functions, the recombination takes place with high probability, resulting in an intense PL emission. Whereas, a very weak PC signal due to the small tunneling rate is observed. With increasing $V_g$, the electric dipole moment is increased because of the electron moving to one interface of the QD and hole to the other. As a result, the recombination probability decreases, correspondingly, tunneling rate slightly increases. Hence, the PL intensity decreases, and PC signal is slightly built up, as shown in Figs. 1(b) and 2. In the meantime, the electrochemical potential of the emitter becomes closer and closer to $E_1$. When the energy level of $E_1$ drops into the bias voltage window, both PL and PC signals start to swiftly change. By increasing further...
the reversed bias, the electrochemical potential of the emitter starts to approach the energy levels of \( E_{12} \) and \( E_{21} \). Afterwards, the energy levels of \( E_{12} \) and \( E_{21} \) will also successively fall into the bias voltage windows. Since the bias voltage makes the difference \( \Delta E \) between \( E_{21}^{(2)} \) and \( E_{11}^{(1)} \) larger and larger, the \( E_{21} \) approaches closer and closer to \( E_{12} \). For a certain value of \( V_{b} \), the \( \Delta E \) will then reach \( \Delta E_{p} = E_{21}^{(2)} - E_{11}^{(1)} \) induced by the coupling between lateral QDs, resulting in alignment of the levels \( E_{12} \) and \( E_{21} \). Hence, the condition of SET is fulfilled, inducing further enhanced PC signal. Therefore, the PC curve exhibits steps reminiscent of SET. Correspondingly, the step-like behavior also emerges in PL curves. Since both the separation and size of QDs influence the coupling between lateral QDs, the behavior of PL and PC depends on the detection energy, as shown in Fig. 1(b).

Figure 4 shows the PL intensity as a function of energy for three different applied voltages. It is noted that under small reverse bias voltage (\( V_{b} = -0.97 \) V), the PL intensity only slightly decreases. By increasing the reverse bias, the PL intensity variation becomes larger and larger. In addition, the higher the detection energy is, the larger the PL intensity changes. At the smallest detection energy, a crossing among the three curves takes place. They imply that carrier tunneling depends on the QD size. The probability of tunneling and escape rate of electrons out of the small dot subset is high due to the more shallow nature of the confined electron level as compared to that of the large dots. This provides further evidence for our charge transfer model described in previous paragraph.

In summary, we have observed a detection-energy dependent anomalous increase in the PL intensity of self-assembled five-layered InAs/GaAs QDs with increasing reverse bias voltage, which also consistently manifested in the complementary PC measurement. We attribute this additional feature, in comparison to the PL (PC) behavior of a single quantum dot, to the interplay between the coupling of lateral QDs and tunneling among vertical ones.

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Electric field effects on the spatial energy transport in self-assembled quantum dots

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Abstract
The spatially resolved energy transfer process in a quantum dot system submitted to electric fields has been measured by a photoluminescence (PL) confocal technique. Strong dependence of the PL spatial width upon the applied electric field of the junction was observed at low temperatures. The carrier system dynamics have shown a high PL background, due to the effect of accumulation of photons trapped in the QD layer structures, also showing distinct emission energies beyond the laser excitation region even at relatively high electric fields. The size of the PL emission region is linearly proportional to the excitation intensity. The spatially resolved measurements demonstrate both the mechanisms of photon recycling and the amplified spontaneous emission.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Quantum dot (QD) structures have been the subject of intense searches for the discrete and zero-dimensional electronic state. Motivated by their excellent opto-electronic quality and their favourable characteristics, self-assembled InAs-GaAs QDs are potential candidates for novel applications such as memory devices [1]. Electronic and optical properties and manipulation have great potential in spintronics and quantum information processing. One of the most critical needs in developing quantum gate implementations is to obtain controllable interaction between qubits [2]. The interaction between two qubits states as well as those for two excition qubits results from carrier tunneling between dots and Coulomb interactions [2–4]. Consequently, the charge transfer problem in QD structures under applied electric field is highly important to understand the structure dynamics and its real applicability for devices.

Although the occurrence of charge transfer between neighbouring QDs is known in the literature [1–9], the mechanisms that allow such transfer are not yet completely understood. In the high temperature regime (T > 90 K), the energy transfer phenomena is correlated with the redistribution of carriers between QDs assisted by thermal activated process [5–7]. As the temperature increases, the carriers confined in smaller dots are thermally activated to the wetting layer and surroundings, thus recombining in larger dots as the recombination energy is smaller. In CdSe nanostructures for instance, the excited energy transfer mechanism is described by a radiationless transfer given by dipole–dipole interactions such as Förster-type energy transfer [8, 9]. In InAs-GaAs QD samples, with average distance between dots smaller than 10 nm (tunnelling time smaller than recombination time), the transfer mechanism occurs by tunnelling. However, several studies [10, 11] have indicated an energy transfer even in samples with distance between dots larger than 10 nm, where the tunnelling time is larger than the recombination time. Accordingly, the energy transfer among neighbouring dots would involve a connection through a continuum of states of wetting layer [12]. In InAs-GaAs QD layers, with separation larger than 10 nm, an energy transfer process between dots was successfully described by an amplified spontaneous emission (ASE) [13].

In this paper, we shall study the energy transfer process between InAs QDs using vertical electric fields from a p-i-n junction. By using a confocal microphotoluminescence technique we measured the spatial width of the photoluminescence (PL) in order to observe the energy spatial transfer in the QD system. The signature of an ASE process could be observed at relatively higher field intensities and lower temperatures.
2. Sample design and experimental details

The sample studied was a GaAs p-i-n diode structure grown by molecular-beam epitaxy at 500 °C with a single layer of InAs dots embedded at the centre of the 300 nm GaAs intrinsic region. The dots were formed from 2.4 ML of InAs deposited at 0.01 ML s⁻¹ using the Stranski–Krastanow growth, and had a density $3.5 \times 10^{10}$ cm⁻², 8 nm height and 18 nm base length. Mesas with 400 μm diameter optical access were employed. The electric field ($F$) in the intrinsic region (width = $w_1$) of a p-i-n structure is controlled by the applied bias ($V_A$) and the built-in junction potential ($V_B \sim 1.5$ V for GaAs p-i-n diodes), according to the relation $F = (V_B - V_A)/w_1$, where $V_A < 0$ corresponds to reverse applied bias. Figure 1 shows the schematic band structure diagram for a single-layer QD p-i-n diode under applied reverse bias ($V_A$).

The microcoluminescence spectra were recorded using a 0.5 m spectrometer and a liquid-nitrogen-cooled Ge detector. The spatially resolved PL measurements are accessed by scanning the PL image plane using a confocal pinhole attached to translation stages [12, 13]. A carrier gradient is generated in the QD sample by a tightly focused HeNe (~1.959 eV) laser beam, reaching 6 kW cm⁻² for a 5 μm wide spot.

3. Results and discussions

The PL spatial profiles corresponding to the fundamental state energy, 1.10 eV, with the field varying from 0 to 80 kV cm⁻¹ are presented in figure 2. The inset shows the PL emission at a region close to the laser spot collected by the confocal pinhole. Three major peaks of QD luminescence (roughly 1.14–1.29 eV) are detected. Two minor peaks are also observed between 1.10 and 1.35 eV. If the excitation power is elevated from 1 to 100 mW, the intensities of higher energy peaks reach or even exceed the intensities of lower energy peaks. Thus, we attribute the multi-peak structures to signals of the ground and excited energy states of electrons in InAs QDs (marked as $I_0$, $I_1$, $I_2$, $I_3$ and $I_4$ in figure 2), the so-called state filling effect. The PL peaks can be fitted to Gaussian functions, the full-widths at half maximum (FWHMs) being 52.4 meV, 46.8 meV, 43.4 meV and 42.0 meV, for $I_0$, $I_1$, $I_2$, $I_3$ and $I_4$, respectively. The peak at 1.44 eV always appears in low density QD samples and has been assigned to the wetting layer. The peak at 1.48 eV corresponds to the GaAs barrier layer.

A Gaussian function in the spatial measurements is used to fit the distribution whose width depends upon the employed wavelength and the optical excitation intensity. The PL spatial width ($\Delta$) is defined as the full width at half maximum (FWHM) from the spatial distribution. The FWHM of the laser spot (not shown) was set to 5.0 μm. In figure 2, the PL profile as a function of the applied field is overlapped by a large background that practically extends over the whole mesa, mainly at low fields. In the absence of the field, $\Delta$ is approximately 77 μm. By using the same steps, the first ($I_1$) and the second ($I_2$) excited states have demonstrated quite similar profiles, not shown in the figure, with $\Delta(I_1) = 32$ μm and $\Delta(I_2) = 17$ μm. The small asymmetry on the right-hand side of the distribution at 100 μm probably corresponds to defects or inhomogeneities in the QD distribution. The PL emission intensity from the first and the second excited states grows with the excitation intensity although the fundamental state ($I_0$) saturates. The PL spatial profile is much larger compared with the spot size, thus the hypothesis for spatial energy transfer in the QD layer is highly supported. Furthermore, according to this picture there are more evidence: the energy transfer is more effective without applied field plus the transfer to lower energy states is more effective when compared with higher excited states.

Since energy transfer by tunnelling is unlikely to happen between adjacent QDs with average neighbour distance of approximately 40 nm, we must expect relatively low-tunnelling rates. In other words, the tunnelling times become longer compared with the characteristic carrier lifetimes in QDs. In this study, the hypothesis of energy transfer through the wetting layer must be taken into account, as previously described [13]. In order to check this hypothesis, $\Delta$ was measured as a function of the temperature as shown in figure 3. The width $\Delta$ decreases significantly as the
Figure 3. PL spatial width ($\Delta$) in the absence of applied field as a function of the sample temperature for the states $I_0$, $I_1$, and $I_2$. The lines are only to guide the eyes.

Figure 4. PL spatial width $\Delta$ as a function of the excitation intensity corresponding to the states $I_0$ (open symbol) and $I_1$ (closed symbol). The best fittings follow $\Delta \propto I_{exc}^{1/2}$, where $I_{exc}$ is the laser excitation intensity.

As the temperature increases, thus the energy transfer process may become clearer when thermal effects are not disregarded, as carriers are transferred to higher energy levels and to the wetting layer [14]. The decrease in $\Delta$ is first confirmed by a low number of carriers in the lower energy levels, and second, thermally activated processes in these levels work as a main quenching factor. In the same way, the effect of carrier loss in the excited levels with a relatively larger number of carriers is less noticed with the increase in the temperature. Although the carriers vanish by thermal activation, many still recombine radiatively in the dots. Therefore, as expected, the results demonstrated that thermally activated energy transfer is highly supported in order to describe the overall carrier migration in the QD system.

In order to understand the fundamental mechanisms for energy transfer in the QD system, we also measured and plotted $\Delta$ for the fundamental $I_0$ and first excited $I_1$ states as a function of the excitation intensity (see figure 4). We found that $\Delta$ grows as a function of the square root of the excitation intensity. This reminds that the luminescence emission area (Area $\propto \Delta^2$) grows linearly with the excitation intensity. Energy transfer enhancement in the regime of high excitations can be explained by excess of excited carriers photogenerated in the highly focused region of the sample. Excited carriers relax afterwards losing energy as phonons until they are captured by lower energy levels. Further relaxation from low-energy states emits photons, although only a small fraction of generated photons escape from the sample due to the small critical angle for total internal reflection. Then, a considerable amount of light is reabsorbed and reemitted before it leaves the sample, creating a photon cascade outside the excitation region. Higher energy photons are quickly absorbed at the points near the excitation region. Consequently, the migration range of these photons is spatially limited. On the other hand, the absorption of low-energy photons is lower, but their spatial range is larger.

To understand the high-energy transfer efficiency from $I_0$, at low fields, we just need to remember that the gain region corresponding to $I_0$ grows quickly following the relaxation of confined carriers in $I_1$, located in the vicinity of this region. While the gain region corresponding to $I_0$ increases, the one corresponding to $I_1$ decreases. Another feature is that the gain region may become transparent to the excess of photons generated in the excitation spot, thus photons migrate to the boundaries of the transparent region whereby they are absorbed. At the same time, both the total area corresponding to the PL emission region and the transparency region increase with the excitation intensity. The boundary of the mesas limits the spatial range for migrating carriers. When migrating photons reach the edge, they either reflect back or escape the mesa according to the refractive index differences. The consequence of this fact is the confinement of carriers inside the mesa observed through the background level shown in figure 2.

Figure 5(a) shows the PL intensity as a function of the junction applied field. For comparison, we plotted the energy transfer parameter $L$ in figure 5(b) using the relation $L = (\Delta - \Delta_0)/2$, where $\Delta_0$ is the excitation spot width for the fundamental (open symbol) and first excited states (closed symbol) as a function of the electric field. At low fields ($E < 7$ kV cm$^{-1}$) there are several allowed states for recombination, corresponding to small changes in the PL intensity. By increasing the field carriers inside the QDs may find distinct recombination channels at allowed states besides the tunnelling process. The tunnelling times are highly dependent on the electric field [16]. Tilting of the bands favours the increase in tunnelling probability to the contact regions (figure 1). In figure 5, at 25 kV cm$^{-2}$ approximately, the luminescence intensity drops quickly. Competition with other processes is ruled by the action of the field. Certainly, the electron radiative lifetime in a QD (typically 1 ns) corresponds to approximately the electron tunnelling time [17]. Thus, as the field increases more electrons escape from the dots and the luminescence intensity quenches quickly. There is a strong relation between $L$ and the PL intensity in a given state. The spatial width $\Delta$ depends on the photon current in the QD layer direction, and also depends on the confined carrier density. The net result is the weakening of the luminescence on the measured states, which corresponds to smaller spatial width. Therefore, $L[I_1]$ is approximately three times smaller compared with $L[I_0]$ (see figure 5). On the other hand, the luminescence intensity corresponding to $I_1$, in the excitation region, is approximately 1.5 larger than $I_0$ in the same field range. The energy transfer mechanism as a function of the QD...
density was investigated by Sales et al. [13] in QD samples with low and high QD densities through the investigation of the spectral, spot size and excitation intensity dependence of the PL spatial width.

Due to the competition between the generation of photons and the tunnelling caused by the electric field, it is possible to control the photon flux from the excitation region. If such flux is high enough to fill in half the less energetic states of the QDs, the optical absorption will tend to zero, which corresponds to the transparency regime, and the photons do migrate further. Decreasing the field influence, such spread will increase until it reaches a distance where the photon flux cannot override the losses.

In essence, we observed that energy flows out of the excitation region and reaches further out. At least in the transparent region half the QD states are loaded. If there are photons travelling in this region, they stimulate carrier recombination in confined states that can start stimulated emission. Following population inversion to the excited states, this leads us to believe that an energy transfer is being driven by an ASE process. In order to properly check the ASE possibility, we measured the PL spatial width for the states $I_0$ and $I_1$ as a function of the spot size. To do that, in figure 6, the excitation intensity was maintained constant as the laser spot size increased. A superlinear behaviour of $\Delta$ was observed, which is more pronounced in the state $I_0$. However, this behaviour is not expected in the case of a conventional diffusion process. In zero-dimensional systems the radiative recombination mechanisms grow linearly with carrier density, and for this reason the PL spatial profile does reflect the proper spatial profile of the carrier density [6]. If optical gain is present, the outward photon flux from the excited region increases with the distance travelled by the photons in the gain region. Therefore, as the excitation spot is increased in diameter, while the average power is kept constant, the radial photon flux resonant with QD states will be amplified and be absorbed in the outer unexcited rim. If the flux is strong enough such that half of the QDs in this newly excited region are in the excited state, then the optical absorption is brought to zero and the photons reach further outwards. The photons will then make their way outwards up to a distance where the incoming flux cannot overcome the losses. This implies that, for a constant excitation spot size, the size of the luminescence spot should increase with the excitation intensity. In the same way, we should also expect it to increase with the excitation spot size for a constant excitation power, since the size of the gain region is increased.

To explain the photon recycling, excited carriers relax after losing energy as phonons until they are captured by lower energy levels. Further relaxations from low-energy states emit photons, although only a small fraction of generated photons escape from the sample due to the small critical angle for total internal reflection. Then, a considerable amount of light is reabsorbed and reemitted before it leaves the sample, creating a photon cascade outside the excitation region.

4. Conclusion

A PL confocal technique has been used to measure the spatially resolved energy transfer process in a QD system, demonstrating both the mechanisms of photon recycling and ASE. The results confirmed that an energy transfer model is more effective on the low-energy range of the PL distribution.
A strong luminescent background is verified at different level energies over the entire mesa, even at a relatively high electric field. The background is also due to the effect of accumulation of photons that are trapped in the QD layer structures. A strong dependence of the PL spatial width upon the applied electric field of the junction was observed.

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References

Electric field effects on the carrier migration in self-assembled InAs/GaAs quantum dots

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Abstract: Electron and hole dynamics from self-assembled quantum dots subject to vertical electric fields have been studied by observing the photoluminescence (PL) image on the sample surface. We have observed an asymmetric profile associated to migration of optically excited electron and holes in the quantum dot (QD) structure. The asymmetric profile is increased by rising the applied bias voltage. This behaviour was associated with charge accumulation at different regions of the QD layer plane due to an asymmetric electric field upon which the QDs are immersed.

Keywords: Semiconductor quantum dots, Carrier migration, Microluminescence.

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1. Introduction

Self-assembled InAs/GaAs quantum dots (QD) is one of the most studied system, primarily devoted to applications such as lasers, infrared detectors and memory devices [1-4]. Study of physical process of diffusion, relaxation and recombination has a key importance for the development of devices. Despite great studies of QD devices, the dominant mechanisms for increasing efficiency of photoluminescence (PL) is still not well understood. One suitable technique to understand the dynamics of optical absorption in QD is the photocurrent spectroscopy, which can give information about the mechanism of capture and escape carriers [5, 6].

We report on the electron and hole dynamics in InAs/GaAs QD heterostructures by means of spatially resolved PL [7]. We show that the PL spatial profile can be manipulated by biasing the device. We found experimental evidence of a dynamical process of charging and discharging with photogenerated holes and electrons. This has an important role in determining the tunnelling rates that affect the profile of the luminescence on the sample surface. It is pointed out that charge accumulation may occur close to the contacts of the QD structure. We present a qualitative analysis that explains the observed behaviour.

2. Sample structure and experimental details

The sample studied was a GaAs p-i-n diode structure grown by molecular-beam epitaxy (MBE) with one layer of InAs dots. The sample was grown on n+-doped GaAs (001) substrate, upon which a contact layer of n+-doped GaAs was deposited. This was followed by a layer of nominally undoped GaAs. The QDs were formed with the Stranski-Krastanow technique by depositing 2.4 monolayers (ML) of InAs at ~500°C,
using a growth rate of 0.01 ML/s. The dots were subsequently overgrown with a second undoped GaAs layer and capped with a p'-doped contact layer. From plan-view Transmission Electron Microscopy (TEM) the estimated areal density of the dots is \(-3.5 \times 10^{10}\) cm\(^{-2}\), base size 18 nm and height 8.5 nm [8]. The device were lithographically processed into 200 \(\mu\)m radius circular mesas and metalised with a gold-germanium annular top contact. Conducting gold-epoxy resin was then used to mount the bottom of the substrate onto the head, with the contact bonded with gold wire. The electric field across the intrinsic region is controlled by the built-in potential and the applied bias (\(U\)). Reverse biasing results in an electric field oriented along the growth axis from substrate to surface.

The PL and the spatial resolved photoluminescence (PL) measurements were performed at -198 °C (75 K) using a microluminescence surface scan technique (MSST) [7]. In the MSST a carrier gradient is photogenerated inside the sample through a tightly focused HeNe laser beam onto a 3 \(\mu\)m diameter spot with \(E_{\text{exc}}=1.96\) eV. The mesa was illuminated from the topside, and the spatially resolved measurements are achieved by scanning the PL on the image plane using a pinhole (50 \(\mu\)m). We chose two orthogonal directions to perform the scan (x, y directions). The collected light was resolved by a 0.5m monochromator and detected by a nitrogen-cooled Ge detector. The position and focus of the laser beam on the mesa were checked by a CCD camera.

3. Results and Discussion

Generally QDs systems can be treated as a two-level system, assumed to be in level 1, if QD is unoccupied, otherwise it is supposed to be in level 2. If we define two-time averaged occupation numbers \(n_e\) and \(n_h\) in such a way that \(n_e + n_h = 1\), where \(n_e\) and \(n_h\)
are in between 0 and 1, we can well describe our system according to the following two coupled rate equations:

\[
\frac{dn_e}{dt} = G \left(1 - n_e\right) - \frac{n_e}{\tau_e} - \frac{n_e n_h}{\tau_R} \tag{1}
\]

\[
\frac{dn_h}{dt} = G \left(1 - n_h\right) - \frac{n_h}{\tau_h} - \frac{n_e n_h}{\tau_R} \tag{2}
\]

, where \(\tau_e\) and \(\tau_h\) are tunnelling times for electron and hole and \(G\) is generation rate.

Since the tunnelling times for both electron and hole strongly depend on the electrical field, the resolution of rate equations, i.e., density of electrons and holes inside QDs, will also depend on electric field. The Wentzel-Kramers-Brillouin (WKB) approximation is used to estimate the values of \(\tau_e\) and \(\tau_h\), which strongly depend on the barrier height. For a 1D confining potential with width \(L\) in a perpendicular field \(F\), the tunnelling rate \(R_T\) is given by:

\[
R_T = \frac{\hbar \pi}{2 m L^2} \exp \left[ -\frac{4}{3 \hbar e F} \sqrt{2 m E_i} \right] \tag{3}
\]

, where \(E_i\) is the ionisation energy of the electron eigenstate. Superimposed to the external electric field (applied bias), there is an internal field component corresponding to \(V_{in} \sim 1.5\) V due to the charge distribution through the diode structure. The relation between the applied bias and the total effective electric field \(F\) experienced by the carriers require a self-consistent calculation. We consider an average effective field that qualitatively accounts for the main effects of the PL emissions and photocurrent, i.e.,

\(\bar{F} = F_0 + \Delta F\), with \(F_0 = (V_{ap})/d\) and \(\Delta F = (n_h - n_e) e N_{\text{QD}}/\varepsilon_0 \varepsilon_r\), where \(\varepsilon_r\) is the static
dielectric constant for InAs, $N_{QD}$ is the QD density and $d$ is the width of the intrinsic region.

Figure 1 demonstrates the PL spectrum of the sample showing the ground and excited states of the QDs and the GaAs barrier emission peak. Our spatial PL measurements are performed by tuning the spectrometer at the QD main peak located at 1.13 eV, and also at the GaAs peak located at 1.51 eV. The results are shown in Fig. 2. This figure displays the QD PL profile (solid line) and the GaAs PL profile (dashed line) on the sample surface by scanning the x- and y- directions crossing the centre of the laser spot (dotted line). Note that the peak of QD PL profile shifts (y-direction) compared to the laser spot, even without applied bias (open circuit). The GaAs PL profile clearly does not shift with the applied bias, and is quite useful to locate the centre of the photogenerated carrier distribution. The built-in potential ($\sim$1.5 V) is not constant along the QD layer plane due to a non-homogeneous distribution of the gold-germanium contacts; consequently it induces an asymmetric modification of the QD lateral confining potential. The observed shift is the evidence that the electric field potential profile is asymmetric inside the mesa.

In Fig. 3, two main effects are observed by raising the applied bias: the QD peak shifts to left and its intensity increases. The PL intensity quenches on the metallic contacts. In the x-direction on the left-hand side the quenching of PL intensity is due to the metallic region. The two small peaks on the left-hand side were generated by the imperfections (holes) on the contact surface.

In order to investigate the electric field effects upon the QD PL profile, we measure the confining charges inside the dots. At direct electric fields ($U > 0$ V), the holes as
well as the electrons stay in the QD and recombine. At high reverse bias \((U < 0 \text{ V})\), the electric field is strong enough to make the potential barrier thinner separating the optically excited electron-hole pairs, since electrons and holes tunnel out of the QDs at different rates [9-12]. Since the top contact is not uniform, the net result in a non-uniform distribution of the confining potential along the QD layer in the mesa structure. The asymmetric profile of the resulting electric field causes an asymmetric carrier migration as a function of the applied bias. It is quite reasonable to think that the optically excited charges are attracted to the direction of lower confining potentials, which means that they can accumulate in the vicinity of the metallic contacts. However, the metal penetration of the contact into the semiconductor layer screens the built-in field in the nearby region, thus the QD band profile may become almost flat. While the band profile becomes flatter, the escape rate of electrons and holes decreases considerably. Consequently, electrons and holes created in the laser spot travels in the GaAs layer and recombine preferentially into the QDs close to the contact region.

The peak shift of the PL profile at zero fields may also be regarded as charge migration and recombination at different regions of the QD structure. This is shown both in Figs. 2 and 3 regarding to the y-direction. Due to the rapid loss of optically generated carriers, the PL signal quenches almost totally on the laser excitation region. The carrier migration occurs in the low confining potentials related with the built-in field. For this reason, even when the applied field is zero we expect that the charges recombine preferentially into the QDs in the vicinity of the contacts.

By applying the bias \((U > 0)\) tunnelling of electrons from the back contact into the ground and first excited QD levels occurs. At this time, the tunnelling rate out of the
QDs becomes much lower. The internal field gets stronger with the bias close to the contact region, and the confining potential of the QDs decreases further, resulting in an intense increase of carrier migration in the GaAs layer from the excitation spot into the direction of the contacts. It has also been observed that at reverse bias, in an intermediate range (-1V < U < 0), no shift is observed. There is no evidence of charge accumulation in the contacts and the tunnelling time should be the same for all QDs in the same layer.

4. Conclusion

We have investigated the spatial PL distribution of optically excited electron-hole pairs in QDs under different electric fields. The QD PL image shifts away from the laser spot. This demonstrates the lateral migration and recombination of carriers in the direction of the contact layers, affecting and competing with the local recombination into the QDs.

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References


Figure captions:

Fig. 1. PL spectrum of the InAs/GaAs QD structure.

Fig. 2. PL intensity profile of the QDs (solid line) on the surface of the mesa, and the GaAs PL profile (dashed line), compared with the laser excitation spot (dotted line), (a) x-direction scan, (b) y-direction scan.

Fig. 3. PL intensity profile from QDs as a function of applied bias (0.0, 0.1, 0.5, 0.8, 1.0, 1.3, 1.5 Volts). The contact layer boundaries can be located as the PL intensity quenches totally.
Figure 1

$T = 75\ \text{K}$
$E_{ex} = 1.96\ \text{eV}

GaAs
Figure 2

a) $U = 0$ Volt

b) $U = 0$ Volt
Figure 3
Nonlinear effects of the photocurrent in self-assembled InAs/GaAs quantum dots

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We report photocurrent (PC) and its complemented photoluminescence (PL) investigations of carrier escape dynamics in InAs/GaAs self-assembled quantum dots (QDs) subject to axial electric fields. We found a nonlinear dependence of PC on the laser excitation power. This interesting behaviour can be tuned by bias voltage. Numerical simulation of steady-state rate equations demonstrates the accumulation of holes trapped in QDs is responsible for this nonlinearity. This laser controlled electronic transport would be expected to open many potential applications in optoelectronic devices.

Introduction

InAs/GaAs self-assembled quantum dots (QDs) have attracted widespread interest due to both their atomic and molecular like electronic structure. They are also promising for ultra-low threshold lasers, memories, spintronics devices, and quantum information processing.\(^1\) Photocurrent spectroscopy is a suitable technique which can be used to probe carrier capture and escape mechanisms occurred in self-assembled quantum dots.\(^2\) Fry and his co-authors had made photoluminescence (PL) and its complementary photocurrent (PC) spectroscopy measurements in a single layer InAs/GaAs self-assembled QDs.\(^2\) They claimed that due to the competition between tunnelling and radiative recombination, PL intensity monotonically decreases with increasing reverse bias voltage, and PC signal shows an inverse dependence.\(^2\) Very recently, we found the dependence of PC signal on applied bias voltage for multi-layered self-assembled InAs/GaAs QDs is characterized by an unusual plateau behaviour, which is in strong contrast with the Fry's observation. This indicates that a distinct mechanism determines the dynamics of carrier tunnelling in single- and multi-layered QDs. Although extensive investigations have been done, the understanding of the carrier dynamics of multi-layered self-assembled QDs is still very primarily. This motivated us to make a systematic experimental and theoretical investigation. In this letter, we present our low temperature PC and PL investigations about the sample consisted of five layers of InAs dots, and report our finding on nonlinear dependence of PC signal. A physical model calculation which shows a well agreement with experimental observation is also presented.

Experimental set-up

The sample studied was a GaAs p-i-n diode structure grown by molecular-beam epitaxy at 500°C with five layers of InAs dots well separated by 20 nm of undoped GaAs. The dots were formed from 2.4 ML of InAs deposited at 0.39 ML/s using Stranski-Krastanow technique, and had a density of about 5x10^{10} cm^{-2}. The electric field \(F\) across the intrinsic region is controlled by the built-in potential \((V_{bi})\) and the applied bias \((V_{b})\). Mesas with 400μm were employed. The sample was mounted in a variable temperature cryostat coupled with the measurement system. The measurements were carried out using a standard lock-in technique. For the PL measurements the emitted light was dispersed by a 0.8m spectrometer and the PL signal was detected by a liquid-nitrogen-cooled Ge detector. For the power dependent photocurrent measurements a micro-PL set-up was used. To clarify the mechanism of carrier
dynamics of tunneling, two kinds of excitations were adopted. Firstly, the sample was excited by a HeNe laser with energy of 1.94 eV. In this case, the electron-hole pairs are created in the barrier region of a QD. Secondly, a Ti:sapphire laser with the excitation energy of 1.3 eV by which the electron-hole are resonantly generated inside the QDs, was employed. Since only the QDs in the contact region significantly contribute to the PC signal, it was possible to chop the laser beam and to measure the modulated signal with a lock-in amplifier.

**Experimental Results**

Fig. 1 shows the intensities of the PL and PC against applied bias voltage for an excitation energy $E_{ex} = 1.94eV$ and a power density of 6W/cm$^2$ at $T=10K$. It is noted that when $V_b$ changes from 0.5 to -0.3 Volts, the PL intensity shows only a very slight variation. With further increasing reverse bias voltage, it decreases swiftly. For bias around -0.7 V, however, PL presents a plateau. After that, it decreases again. When the reverse bias voltage is larger than 1.5 Volts, the PL spectrum is completely quenched. Interestingly, it is noted that the PC signal shows an inverse dependence, which indicates that the competition between tunnelling and radiative recombination occurred. Hence, by varying the field we can control the rate of tunnelling and radiative recombination, i.e. the carrier dynamics.

![PL intensity and Photocurrent signal](image)

**Fig. 1.** PL intensity and Photocurrent signal as a function of bias voltage for an excitation energy $E_{ex} = 1.94eV$ and a power density of 6W/cm$^2$.

The most intriguing results were found when the sample was illuminated by different power density. Figure 2 demonstrates the photocurrent signal of the sample excited by a Ti:sapphire laser versus excitation density for four different bias voltages. It is noted that the dependence of the photocurrent on the power density can be tuned by bias. For the bias voltage $V_b=0$ and -5 V, PC signal presents a linear dependence of power density. For the other values ($V_b=-0.9$ and -1.3 V), however, the nonlinear behaviour is found. Moreover, the characteristics of nonlinearity depends strongly on the bias voltage.

![Photocurrent signal as a function of excitation density](image)

**Fig. 2.** Photocurrent signal as a function of the excitation density for four different bias voltages.

**Physical model and discussion**

The carrier dynamics inside a QD as a function of excitation power and applied bias voltage can be described by fundamental rate equations. In our model, we assume that the QD is a two-level system, and it is assumed to be in level 1, if QD is unoccupied, otherwise it is supposed to be in level 2. We define two time-averaged occupation numbers $n_e$ and $n_h$ in such way that $n_e + n_h = 1$, here both $n_e$ and $n_h$ are in-between 0 and 1. According to the theory of two-level systems, the dynamics of $n_e$ and $n_h$ are governed by the following two coupled rate equations:

$$\frac{dn_e}{dt} = \frac{G}{\tau_e} \left( 1 - n_e \right) - \frac{n_e}{\tau_e} - \frac{n_e n_h}{\tau_R}$$

$$\frac{dn_h}{dt} = \frac{G}{\tau_h} \left( 1 - n_h \right) - \frac{n_h}{\tau_h} - \frac{n_e n_h}{\tau_R}$$

(1)

(2)
where, $\tau_e$ and $\tau_h$ are tunnelling time for electron and hole, $G$ is generation rate. The Wentzel-Kramers-Brillouin (WKB) approximation was used to estimate the values of $\tau_e$ and $\tau_h$, which strongly depend on the barrier height and are mainly determined by the $z$ part of the wave function [Kuo, 2000]. For a 1D confining potential with width $L$ in a perpendicular field $F$, the tunnelling rate $R_T$ is given by:

$$R_T = \frac{h \pi}{2 mL^2} \exp \left[ -\frac{4}{3} \frac{h e F}{2 m E_i^3} \right], \quad (3)$$

where $E_i$ is the ionisation energy of the electron eigenstate. Then the tunnelling times ($\tau_e$, $\tau_h$) can be calculated from Eq. (3). Superimposed to the external electric field (bias), there is an internal field component corresponding to $V_{in} \sim 1.5\text{V}$ due to the charge distribution throughout the diode structure. The relation between the applied bias and the total effective electric field $F$ experienced by the carriers would require a selfconsistent calculation. We consider an average effective field which qualitatively accounts for the main effects of the inversion asymmetry on the PL emissions and photocurrent, i.e., $F = F_0 + F_i$, with $F_0 = (V_n-V_h)/d$ and $F_i = (n_h-n_e)\varepsilon_r \text{QD}/d$, where $\varepsilon_r$ is the static dielectric constant for InAs and $d$ is the width of the intrinsic region. In the steady state regime, the coupled Eq. (1) and (2) together with the tunnelling times ($\tau_e$ and $\tau_h$) have been solved self-consistently.

Figure 3 demonstrates our calculated dependence of the normalized charge-density difference between electrons and holes for four different excitation-powers. The Gaussian type curves were found for all of the four cases. In another words, for a given excitation power, at both lower and higher regimes of bias, there is no net charge found inside a QD. For a certain interval of bias voltage, however, the positive charge accumulation takes place. Fig. 4 shows our theoretical prediction about photocurrent as a function of excitation power for different bias voltages. It is noted that a very good agreement between theoretical calculation (Fig. 4) and experimental observation (Fig. 2) is achieved.

According to our theoretical prediction, the underlying physics of nonlinear behaviour of PC and PL shown in Fig. 1 and Fig. 2 can be interpreted as follows. In the PC and PL measurement of Fig. 1, the electron-hole pair is firstly created by the HeNe laser excitation in the GaAs barriers in the contact region. Then they may be captured by one of their nearby QDs. After that, they relax from the higher energy levels to the ground state of the QD, accompanied by phonon emission, forming an exciton. Finally, the electron may recombine with the hole, emitting a photon, or they may escape from the dots, giving rise to PC signal. In the regime of

![Fig. 3. Variation of the net charge density as a function of bias voltage at four different excitation powers.](image)

![Fig. 4. Computed photocurrent as a function of excitation power for different bias voltages.](image)
low electric fields, the electrons recombine with the holes inside the QD with a high probability due to a large overlap between the electron and hole wave functions. In contrast, the tunneling rate for both electron and hole is so small that it can be safely neglected. Hence, the strong PL intensity and weak PC signal for Vb from 0.5 to 0.3 Volts are expected, as shown in Fig. 1. As the reverse bias voltage is further increased, the electric dipole moment will be strongly enhanced due to the movement of electron and hole along an opposite direction, driven by applied bias. Then the recombination probability decreases, compensated by an increasing of tunnelling rate. Hence the intensity of PL in the range of bias voltage from -0.3 to decreases, and PC single becomes stronger and stronger. Whereas, because the multilayered self-assembled QDs possess thick tunnelling barriers, the photogenerated carriers have to tunnel through these barriers to reach the electrodes. Thus, the carrier accumulation more probably take place in self-assembled QDs than in their single layered counterparts. Moreover, owing to the relatively large effective mass of the holes, the tunnelling time for the holes out of the dots can be expected to be much larger than that of electrons. Therefore, for a certain interval of bias voltage, the holes are prior to accumulate in QDs in comparison with electrons, as predicted by Fig. 3. It manifests itself in PL and PC curves-emergence of a plateau, as shown in Fig. 1. With a further increasing of reverse bias voltage, the reduced barrier height facilitates carrier tunnelling. Hence, PC increases again, accompanied by a decrease of PL intensity. In the regime of large negative bias, the electron-hole pairs are completely ionised by the electric field before recombination can take place. Therefore, PC becomes saturated and PL is completely quenched.

In analogy with previous analysis, the dependence of photocurrent signal on excitation density can be also well understood. The sample used in Fig. 2 was excited by a Ti:sapphire laser with an excitation energy lower than gap of GaAs barrier. Then the electron-hole pairs were resonantly generated inside the QDs. At low electric fields, the holes as well as the electrons were confined in the QD, and a large overlap between the electron and hole wave functions results in a high-rate radiative recombination. In contrast, the rate of carrier tunnelling is so small that it can be safely neglected. Hence, no net charge density is expected. Accordingly, the photocurrent presents a linear dependence on excitation density. In the regime of high reverse bias voltage (|Vb| > 2 V), the electric force becomes so strong that it can swiftly drive both electrons and holes to completely tunnel out from the QD. Therefore, the net change density becomes zero again. In this case, a linear behaviour of PC is also expected. For the intermediate values of bias voltage, however, the competition between quantum confinements which favour an accumulation of carriers inside QD and quantum Stark effect which facilitates carrier tunnelling may lead to complex nonlinear phenomena of photocurrent. In fact, by increasing the reverse bias voltage, the electric dipole moment is enhanced due to an enlarged separation between the electron and hole, resulting in a reduced recombination rate and an enhanced tunnelling rate. On the other hand, the larger effective mass of holes in comparison with electrons leads to its tunnelling-rate smaller than that of electron. The large tunnelling time favours accumulation of holes inside the QDs, resulting in a net positive charge density. According to our simulation prediction, it is responsible for the nonlinearity of excitation dependence of PC signal.

Finally, from Fig. 3, it is also interesting to note that with an increase of excitation power, the peak position of Gaussian function shifts to larger value of reverse bias, and its line width at half height becomes wider and wider. It indicates that the number of photoreacted electron and hole pairs also impacts the net positive charge distribution function, consequently the nonlinearity of photocurrent. In another words, the nonlinearity of PC signal is determined by the interplay between bias voltage and excitation density. It is clearly demonstrated in both Fig. 2 and Fig. 4, in which the dependence of PC on excitation density is tuned by applied bias voltage.

**Conclusions**
We report on the dynamics of carrier tunnelling in multi-layered InAs self-assembled QDs. Both photocurrent and PL curves show clear nonlinear dependence on excitation density and applied bias voltage. The simulation of rate equations unambiguously demonstrates that the non-linearities are attributed to the accumulation of photogenerated holes inside QDs.

References

Optical properties of CdS nanoparticles embedded in polymeric microspheres

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Abstract
Mesoporous microspheres of styrene-divinylbenzene (Sty-DVB) copolymer have been used as template for CdS semiconductor quantum dots (QDs). Micro-photoluminescence, optical absorption and Raman spectroscopy were used to characterize the optical properties of the CdS QDs. When a single microsphere is excited by a laser beam at room temperature, very strong and sharp whispering gallery modes are shown on the background of PL spectra of CdS QDs, which confirms that coupling between the optical emission of embedded QDs and spherical cavity modes was realized. The results show that the microspheres embedded with CdS nanoparticles work as an optical microcavity allowing the observation of whispering gallery modes. The lasing behaviour is achieved at relatively low excitation intensity at room temperature. High-optical stability and low-threshold value make this optical system promising in visible microlaser applications.

Keywords: photoluminescence, polymeric microsphere, CdS quantum dot, microcavity, nanocrystals

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1. Introduction

Semiconductor nanocrystals quantum dots (NQDs) have attracted a great deal of attention since they can provide a superior performance in lasing applications, and can be used in a broad range of applications such as optoelectronics, telecommunications, sensors, and artificial photosynthesis. The design and synthesis of nanometer-scale particles (specifically, semiconductor nanocrystal-quantum-dot based) have been the focus of intense fundamental and applied research, with special emphasis on their size-dependent properties [1-12].

From fundamental to lasing applications several types of microcavities structures have been used [4-10]. A spherical three-dimensional optical microcavity can be made of a nonabsorbing microsphere with a higher refractive index than the surrounding medium, having a diameter comparable to or slightly larger than the light wavelength, i.e., a few microns [13,14]. In such microcavities, there exist a number of discrete resonant optical modes, the so-called whispering gallery modes (WGM). WGM is a resonance of light wave trapped inside dielectric spheres or disks by total internal reflection. Glass and polymeric microspheres are suitable for optical devices with WGM resonators. Efficient lasing from dye doped polystyrene microspheres has been observed [8,11]. When a single microspherical cavity is excited by a laser beam at room temperature, very strong and sharp resonance peaks appears on the PL spectra, which can be well explained by the coupling of QD luminescence with the WGM of the spherical microcavity based on the Mie scattering theory.

We emphasize the simplicity and flexibility in fabricating polymeric microspheres ranging in diameter from 10 to 100 μm. The mesoporous styrene-divinylbenzene (Sty-DVB) copolymer were used as a template to embed the NQDs. Our ion-exchange method simplifies control of the density of NQDs deposited on the microsphere. II–VI semiconductor compound such as CdS was chosen for QD emission, and we have so far produced lasing wavelengths at 570 nm.

In this work, the NQD luminescence can couple with the WGMs, and a lower threshold of stimulated emission or lasing modes of QDs may be realized. NQDs are predicted to provide superior performance in lasing applications in comparison with bulk and other low-dimensional semiconductors, due to the discrete structure of optical transitions, inhibiting the thermal depopulation of the lowest “emitting” states. By combining the advantages of a microspherical resonator with optical stability and a QD gain medium, we take another step toward achieving microlasers with low threshold values and high efficiencies [4,7].
2. Sample and experimental details

To characterise the CdS nanoparticles embedded in the polymeric microspheres, microphotoluminescence (µ-PL) and Raman spectroscopy have been realized. Optical absorption was obtained at room temperature using a spectrophotometer operating between 250 and 1000 nm.

The Sty-DVB copolymer used in this study was synthesized by suspension polymerisation in the presence of inert diluents [15,16]. Apparent density (0.44 g/cm³), surface area (140 m²/g), average pore diameter (13 nm), toluene regain (1.52 cm³/g), heptane regain (1.24 cm³/g), percentage of volume swelling in toluene (100%), and percentage of volume swelling in heptane (58%) were parameters used to characterize the spherical, micrometer-sized polymeric template. Sulphonation of the Sty-DVB spheres were performed using concentrated sulphuric acid (2 g of polymer/30 mL of sulphuric acid). The reaction was carried out in the presence of dichloroethane (40% in volume with respect to sulphuric acid). The Sty-DVB spheres were first suspended in dichloroethane for a few minutes. Then, sulphuric acid was added slowly while the temperature was maintained at 70 °C for 4 h. The Sty-DVB polymer microspheres were separated by filtration, washed thoroughly with deionized water, and dried at 60 °C for 24 h. The ion-exchange capacity (4.8 mmol of H⁺/g) was determined as described in the literature [17]. CdS nanoparticles were embedded into the microspheres by ion exchange. The microsphere used in the PL experiments showed a perfect surface with a diameter of 10 to 100 μm.

A schematic representation for the micro-PL experiment is shown in Fig. 1. A CW argon-ion laser beam working at the excitation wavelength 514 nm and excitation power at 10 mW is focused onto a spot of about 3 μm on the sample surface using a microscope objective (10x), but due to the spherical shape, the beam becomes tightly focused inside the sample, providing a spot as low as 1 μm wide. The incident laser beam hits the surface and excites electrons in the QDs. Electrons return to the ground state by emitting photons. Emission from the excited microsphere is collected through the same microscope objective. A beam-splitting prism is used to reflect the light back from the sample towards the scanning monochromator. A Spex 750M is used to determine the microlaser emission wavelengths, and a CCD camera operating at 140 K was used to measure the PL intensity.

Raman scattering spectra of the micrometer-sized polymeric microspheres embedded with CdS nanoparticles are measured in a backscattering geometry by using a Jobin Yvon triple micro-Raman system. CW argon-ion laser was used operating at the wavelength 488.0 nm and power of 50 mW. The scattered light was detected by a CCD camera. A 50x objective focused the laser light onto the microspheres. To reduce auto-focalisation inside the sample that may damage it, we had to work at low laser intensities.
3. Experimental results and discussions

Figure 2 demonstrates the PL emission and optical absorption obtained by exciting an ensemble of microspheres. The spectral distribution demonstrates low size dispersion related to the Cds nanoparticles. The Cds nanoparticles exhibit band-to-band absorption centred at 2.48 eV (500 nm). Using this information the nanoparticles sizes were determined from the absorption onset by the effective mass model approximation [2]:

$$E \approx E_{\text{bulk}} + \frac{\hbar^2 \pi^2}{2eR^2} \left( \frac{1}{m_e m_0} + \frac{1}{m_h m_0} \right), \quad (1)$$

where $E$ is the band gap of the nanoparticles, $E_{\text{bulk}}$ is the band gap of the bulk material, $R$ is the particle radius, $m_e$ and $m_h$ are effective masses of the electrons and holes, respectively, and $m_0$ is the free electron mass. With the effective masses of electrons ($m_e = 0.21 m_0$) and holes ($m_h = 0.8 m_0$), we have obtained 14 nm (diameter) for the Cds nanoparticles.

The Raman spectrum of the microspheres is shown in Fig. 3, using the 488 nm excitation line of an argon ion laser. The Raman signals from the microsphere sample are strong for the Cds-like longitudinal optical (LO) phonon located at 308 cm\(^{-1}\), in agreement with what expected by the two-mode behaviour of the lattice vibrations in Cds alloy. The large background accounts for the luminescence from the polymeric template.

However, the PL emission changes significantly when we measure a single microsphere (diameter of 40 µm) using the micro-PL setup. This is shown in Fig. 4. The spectral measurements typically indicate multimode laser operation over a narrow portion of the PL spectrum. The spectrometer resolution of 0.01 nm allows us to distinguish individual lasing WGMs. Then, resonances due to the WGM are observed in the emission spectrum and demonstrate effectively the optical properties of the polymeric cavity.

Details of the WG mode structure are shown separately in Fig. 5, after subtracting the Gaussian background curve from the PL spectrum. There is a clear periodical modulation, which we assign to selected optical modes of the spherical microcavity.

It is found that the intensity of the resonance modes is strong enough to emerge from the background emission and the intensities of the resonance modes increase with increasing excitation power, while the background emission intensity does not follow this trend; it became saturated at high excitation power. This makes lasing behavior easy to achieve even at room temperature. Microlaser output power is shown in Fig. 6 as a function of absorbed pump power.

One of the reasons to observe this phenomenon is due to the large interlevel spacing in NQDs, "quantum-confined" excitons are more robust than bulk excitons, allowing one to excite amplified spontaneous emission (ASE) at lower pump levels. Due to the discrete structure of optical transitions in NQDs, thermal depopulation of the lowest "emitting" states is inhibited. Therefore, NQDs are
predicted to provide superior performance in lasing applications in comparison with bulk and other low-dimensional semiconductors. Also, the QND gain medium was combined with an optical cavity that provided efficient positive feedback.

The Q of a resonator mode is defined as the ratio of resonance frequency to mode linewidth, so high Q values imply narrow linewidths and long cavity lifetimes. We have calculated the value of the optical microcavity quality factor $Q$ using the following expression [18]:

$$Q = \frac{h\omega_0}{2h\gamma}, \quad (2)$$

where $2h\gamma$ is the Gaussian fitting to the linewidth of the cavity modes and $h\omega_0$ is the photon energy. At the wavelength of 571.1 nm ($h\omega = 2.17$ eV), the Gaussian fit is about $2h\gamma = 0.0019$ eV. Then, the quality factor is about $Q = 1,142$. From these results we can conclude that by embedding the CdS nanocrystals in the polymeric microsphere cavity, a strong coupling between photonic and electronic states has occurred.

4. Conclusion

In summary, mesoporous microspheres of styrene-divinylbenzene (Sty-DVB) copolymer have been used as a template to synthesize CdS QDQs. This system was used to study the optical properties of the polymeric cavity and the gain medium, allowing the observation of the resonances modes of WGM laser. The lasing behavior is realized at relatively low threshold value. Thus, the high optical stability of this system makes it promising in visible microlaser applications such as telecommunication and chemical sensing.

Acknowledgement

The authors acknowledge financial support from the Brazilian Agencies: Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) and Fundação de Amparo à Pesquisa do Estado de Minas Gerais.

References and Notes

Figure captions

Fig. 1. Optical confocal setup used for measuring the PL of the microsphere.

Fig. 2. Photoluminescence (solid line) and absorption spectra (dashed line) of CdS NQDs embedded in mesoporous microspheres of styrene-divinylbenzene (Sty-DVB) measured at room temperature. The wavelength of excitation was 514 nm, and the power was 50 mW.

Fig. 3. Raman spectrum of CdS nanoparticles embedded in mesoporous microspheres of styrene-divinylbenzene (Sty-DVB) measured at room temperature. The wavelength of excitation laser line was 514 nm.

Fig. 4. Room temperature PL spectra of a single polymer microsphere compared to the PL of an ensemble of microspheres.

Fig. 5. Normalized PL spectrum shows the whispering-gallery modes.

Fig. 6. Room temperature PL spectra of a single polymer microsphere at two excitation powers (2mW and 23mW).
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Semiconductor doped glasses

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This paper reviews some of the interesting applications of semiconductor nanocrystals embedded in glasses. Because of their unique electronic and optical properties, semiconductor quantum dots (QDs) found wide applications in photonics. They are inexpensive and robust material and have attracted a great attention in the application of 1.3–1.5 μm optical communication. Embedding semiconductor QDs in spherical microcavities is also an attractive system both for fundamental physics research in the field of cavity quantum electrodynamics and for its potential application in lasing materials. Energy transfer processes and coupling-strength between nanocrystals can be studied and demonstrated using semiconductor nanocrystals doped glasses. It has been established that an efficient energy transfer occurs between QDs having a significant band gap energy difference, i.e., between dots of markedly different sizes. We demonstrate that a promising way to enhance energy transfer between different subsets of QDs is to red-shift the emission sufficiently far from the host absorption so that self-absorption by the host becomes negligible.

Key words: Energy transfer, Nanocrystal, Quantum dots, Semiconductor doped glass

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1. Introduction

Semiconductor nanocrystals (or quantum dots, QDs) represent a general class of materials that are intermediate between bulk materials and molecular species. Because of the quantum confinement effect, semiconductor nanocrystals exhibit size dependence, molecular-like discrete electronic and optical transitions. It has been considerable research in this field, especially in the optical properties of semiconductor QDs. A number of matrices have been used for the preparation of semiconductor nanoparticles including glasses. These matrices can be viewed as nanochannels that limit the size to which crystals can grow. The properties of the nanocrystalites are determined, not only by the confinement of the host material but also by the properties of the system, which include the internal/external surface properties of the nanocrystals. New nonlinear composite materials can be prepared by doping glasses with semiconductor nanocrystals. By adding their unique electronic and optical properties, semiconductor QDs found wide applications in the optoelectronics. For instance, semiconductor QDs from the IV–VI family, such as PbS, PbSe, provide access to the limit of strong quantum confinement effect, compared to II–VI or III–V semiconductors, and thus offer excellent opportunities for both experimental and theoretical investigations. They are interesting for infra-red application due to their narrow band gap and large exciton Bohr radii.

The large surface area of a nanocrystal and the surrounding medium, such as the capping agent, can have a profound effect on the properties of the particles. Defects within the nanocrystal act as electron/hole traps that can lead to nonlinear optical effects. Thus, many strategies have been used to coat the surface of the QDs with glass. These types of semiconductor doped glass have an improved stability against flocculation, increased quantum yield, and surface ligands. The structural characterization is also of interest for a better understanding of the physical processes underlying the growth of crystallites inside the glass matrix. The average size of nanocrystals can be tailored by controlling the temperature or time of treatment. The major problem is the size dispersion of the crystallites, which is intrinsic to the diffusion process.

2. Structural and intrinsic properties

The first results on the synthesis of molten glass containing PbS and PbSe crystallites were reported by Borrelli in 1994. Later, the synthesis of phosphate glasses containing PbSe nanocrystals, phosphite, silicate, and boron-silicate glasses with PbS nanocrystals, and the synthesis of silicate glasses containing nanocrystals of PbTe were demonstrated as well. Figure 1 demonstrates the room-temperature absorption spectra of PbS QD doped glasses with different QD radii. One of the most important advantages of semiconductor-doped glasses is the low cost to fabricate compared to epitaxially grown glasses.

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techniques such as molecular beam epitaxy. Suitable thermal treatment of a glass containing the chemical components of a semiconductor can precipitate semiconductor QDs with narrow-size distributions with nice properties, such as few substitutional defects, and few dangling bonds. Jain and Lind have prepared nanocrystals of CdS or CdSe nanocrystals embedded in glass matrix.\(^{10}\) These semiconductor-doped glasses samples have demonstrated large optical nonlinearity and a fast response time. Other glass systems have also demonstrated quantum confinement with microcrystallite CdTe semiconductors borosilicate glasses. The microcrystallite sizes are controlled by the heat-treatment time and temperature.\(^{10}\) The size of the QDs can be evaluated using small angle X-ray scattering (SAXS).\(^{15}\) However, the only direct method to observe the shape of the QDs and to evaluate their size distribution is transmission electron microscopy (TEM).\(^{10}\) These techniques are used to allow collecting the main information about the QDs embedded in glass matrix: their chemical composition, crystalline structure, size, and size distribution. For the electronic characterization many techniques have been used exhaustively, such as optical absorption techniques,\(^{10}\) luminescence spectroscopy, Raman spectroscopy,\(^{19}\) and measurements of nonlinear optical response using time-resolved luminescence.\(^{10}\)

The most striking property of semiconductor nanocrystals is the massive changes in the optical properties as a function of the nanocrystal size.\(^ {11}\) As the size is reduced, the electronic excitations shift to higher energy, according to Fig. 2, and there is concentration of oscillator strength into just a few transitions. These basic physical phenomena of quantum confinement arise by changes in the density of electronic states and can be understood by considering the relationship between position and momentum in free and confined particles. For a free particle or a particle in a periodic potential and the crystal momentum \(p_0\) may both be precisely defined, while the position is not. As a particle is localized, the energy may still be well-defined; however, the uncertainty in position decreases, so that momentum is no longer well-defined. The energy eigenfunctions of the particle may then be viewed as superpositions of bulk \(k\)-states. In the extended case, there is a relationship between energy and momentum, and to a first approximation, the change in energy as a function of the size can be estimated simply by realizing that the energy of the confined particle arises by superposition of bulk \(k\)-states of differing energy.

There are two major effects that are responsible for the size variations in nanocrystal properties. First, in nanocrystals the number of surface atoms is a large fraction of the total. Second, the intrinsic properties of the interior of nanocrystals are transformed by quantum size effects. In any material, surface atoms make a distinct contribution to the free energy, and the large changes in thermodynamic properties of nanocrystals (melting temperature depression, solid-solid phase transition elevation) can ultimately be traced to this. The QD radii \(R\) quoted in Fig. 2 can be calculated using a hyperbolic band model:

\[
\frac{(\hbar \omega)^2}{(c^2/\Delta_0)} = \frac{2 \hbar^2 E_L}{m^*} \left( \frac{\pi}{R} \right)^2
\]

by using the room temperature band gap energy of \(E_G = 0.41\) eV and the effective mass of \(m^* = 0.12\) m\(_0\) for PbS.\(^ {22}\)

At the surface of a pure semiconductor nanocrystal, substantial reconstructions in the atomic positions occur, and invariably energy levels lie within the energetically forbidden gap of the bulk solid. These surface states act as traps for electrons or holes and degrade the electrical and optical properties of the material. The chemical process by which these surface atoms are bonded to another material of a much larger band gap is passivation, in such a way as to eliminate all the energy levels inside the gap. The ideal termination naturally removes the structural reconstructions and simply produces an atomically abrupt jump in the chemical potential for electrons or holes at the interface.

Another important feature related to the nanocrystal QDs is the temperature dependence of the gap energy, i.e., \(\Delta E/\Delta T\). Figure 3 shows that the temperature coefficients of electron-hole pair energies in PbS and PbSe quantum dots depend strongly on the size of the nanocrystal QD. By decreasing the QD size the temperature coefficient of the lowest electron-hole pair energy \(\Delta E/\Delta T\) decreases by more than an order of magnitude from the bulk value. The contributions from interband electron-phonon, intraband electron-phonon, envelope thermal expansion, and lattice dilatation are taken into account. Note that \(\Delta E/\Delta T\) becomes slightly negative for smaller QDs according to A. Olkhovets et al.\(^ {23}\)

3. Applications

3.1 Nonlinear phenomena

Semiconductor-doped glasses embedding nanocrystals of CdS or CdSe demonstrate large optical nonlinearity and a fast response time.\(^ {24}\) However, the response time in these glasses
decreases by light irradiation, a process known by photo-darkening effect. Photo-darkening is a photo-chemical process and involves deposition of ions on the existing QDs. This apparent increase in the size of the QDs leads to reduction in nonlinear optical properties, which limits the applications of nano-crystals towards opto-electronic devices. Results also indicate that defects are created by laser irradiation. The photoinduced defects are considered to be due to trapped electrons in the glass matrix. So, they act as nonradiative recombination centers and provide additional channels for the recombination of excited carriers, increasing the decay rate of the luminescence.

After 1997, substantial progress occurred and quite impressive results were obtained, mainly due to the fabrication of glasses colored with narrow band-gap IV–VI semiconductors, the case of PbS and PbSe. The band-gap wavelengths of PbS and PbSe are approximately 3.0 and 4.5 μm, respectively, at room temperature. These might allow excitation absorption bands in the wavelength range 1–3 μm. Glasses containing PbS or PbSe nanoparticles of different sizes were applied as saturable absorbers for near-IR lasers. This means that these materials can be used for both mode-locking and Q-switching of near-infrared solid-state lasers emitting at the wavelengths from 1.0 to 2.1 μm. Passive shutters based on saturable optical absorption allow obtaining light pulses of high power and short/ultrashort duration.

The nonlinear optical properties of PbS QD-doped glasses have been studied recently for mode-locking and gain applications; however, all of these studies have been performed in bulk glasses. Waveguides produced by using semiconductor doped glasses have been produced for integrated photonic devices. CdTe-doped glass has also demonstrated to be able to passively mode lock a Ti:sapphire laser.

Various nonlinear optical techniques, i.e., degenerate four wave mixing (DFWM), non-degenerate four wave mixing, spectrally resolved two beam coupling technique, and single beam Z-scan have been employed to measure the nonlinear optical response of semiconductor doped glasses containing nanocrystals of semiconductors. Miyoshi et al. investigated the femtosecond dynamics in semiconductor-doped glasses using DFWM experiments. They demonstrated two main contributions for the signal: the fast contribution was attributable to the glass matrix, and the slow contribution was attributable to the photogenerated carriers in nanocrystals. One of the applications upon the nonlinear optical properties presented in PbS, PbSe, and CuSe nanoparticles embedded in glass regards to the design of saturable absorbers. The nonlinear properties excited under nonresonant below gap condition was investigated by Tsuda and Cruz in CdS:Se, CdS:Se, semiconductor-doped glass. They mainly observed the optical Stark shift probed with femtosecond optical pulses.

3.2 Lasing in semiconductor doped microspheres

Embedding semiconductor QDs in spherical microcavities is an attractive system both for fundamental physics research in the field of cavity quantum electrodynamics and for its potential application in optoelectronics. Artemyev and Woggon prepared spherical microcavities using a chemical way. They embedded CdSe semiconductor QDs in the poly(methylmethacrylate) microsphere and realized the coupling of electronic and photonic states. Instead, an approach to prepare glass microspheres embedded with CuSe semiconductor QDs, which have a better optical stability than the polymer microspheres, can be used because the latter are often degraded under strong illumination due to the photo-sensitive surface reactions. The glass has a refractive index of 1.5 or larger, being suitable to employ as the microcavity media surrounded by the air. When a single glass microspherical cavity is excited by a laser beam at room temperature, very strong and sharp resonance peaks were shown on the PL spectra, which can be well explained by the coupling of QD luminescence with the whispering gallery modes (WGM) of the spherical microcavity. Figure 4 shows this strong coupling in the PL spectrum of a single microsphere (4.6 μm in diameter) at room temperature existing at 488.0 nm.

In order to prepare the optical microspheres containing semiconductor QDs, Jia et al. have used commercially available glass ingots that are a source material for making optical filter glasses, for example RG 645 or other types in the same series. The glass ingots contain CdO, CdS, and elemental sulfur or selenium in their composition. They are pulverized into small glass pieces, with the size of a few micrometers and sifted by sieves. Employing a specially designed gas burner to heat and blow off micrometer-sized glass pieces, the glass pieces melt at a temperature higher than the softening point and form into microspheres due to the surface tension. The obtained microspheres can still be annealed at certain temperature for several hours in order to form precipitates and grow CdSe,S1−x nanocrystals QDs in the microspheres. The size of the CdSe,S1−x semiconductor nanocrystals depends on the annealing temperature and time. In the semiconductor doped glass microspheres lower threshold of stimu-

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Fig. 4. (a) PL spectrum of a single glass microsphere with CdSe,S1−x QDs. (b) Normalized PL spectrum after subtracting the luminescence background, showing clear WGM. Clear separations between the adjacent peak wavelengths of the resonant WGMs are shown by arrows.
lated emission or lasing modes of QDs may be realized. Reso-
nant WGMs are observed in the glass microspheres with QDs for
the luminescence bands of both excitonic transitions and from
surface defect states of the embedded QDs. High Q-values of
quality factor are realized for these WGMs as well.

4. Energy transfer mechanisms in PbS and PbSe
quantum dots

Communication, coupling, and coherence between quantum
dots have appeared as central themes in numerous scientifi-
cal efforts of present physical and technological interest.43,44 For
instance, in strongly coupled QD assemblies, electronic excita-
tions can, in principle, delocalise across multiple dots leading to
new states described by coherent superposition of individual dot
wave functions.45 An experimental study to evaluate the strength
of coupling between in PbS and PbSe nanocrystal QDs has been
carried out by analyzing the spatially-resolved PL on the sample
surface.43 The investigation of the carrier transfer dependence
against radius clarifies the process of energy transfer between
the nanocrystal QDs. The PbS and PbSe nanocrystal QDs were
synthesized in oxide glasses. The term "photon diffusion length"
is used to determine the strength of interaction among the dots.48

This interesting way became useful to characterize nanocrystal
samples that contain different assemblies of sizes.

The semiconductor QD glass samples, PbS and PbSe, were
fabricated using sulphur (or selenium) doped oxide glass matrix
(SiO$_2$-Na$_2$CO$_3$-Al$_2$O$_3$-PbO$_2$-B$_2$O$_3$) prepared from high purity
powders using SiO as glass former and Na$_2$CO$_3$ to reduce the
melting point.49 The mixture was then melted in an alumina
 crucible at 1200°C for 30 min. Then, it was cooled down to room
temperature. Thermal treatment of the glass matrix was per-
formed at 500°C to enhance the diffusion of Pb$^{2+}$ and S$^{2-}$ (Se$^{2-}$)
ions. As a result of the thermal treatment PbS (PbSe) QDs were
formed in the glass matrix.

In Fig. 5, the photoluminescence (PL) and the optical absorp-
tion (OA) spectra of PbS and PbSe quantum dots at room tem-
perature can be observed.49 Using these data nanocrystal sizes
were estimated by calculating the exciton energy as a function
of radius for the fundamental state (1sh-1se).49 Particularly, it is
observed a Stokes shift of 140 meV (30 meV) between the PL
and OA peaks of PbS (PbSe) dots corresponding approximately
to 12% (5%) of the recombination energy.

In order to perform the spatially resolved microluminescence,
the samples were mounted in a variable temperature cryostat
coupled with the measurement system. The idea lying behind
this technique is to excite the sample surface using a tightly
focused Ar$^+$-ion laser beam (spot diameter averaging 3 μm
wide). For PL measurements the emitted light was dispersed by
a 0.5 m spectrometer, and the PL signal was synchronously
detected by a nitrogen-cooled germanium detector. The energy
transfer accounts for a broad luminescent region that surrounds
the laser excitation spot. The magnified image of the luminescent
region is scanned by the detection system attached to step motors
and recorded as a function of the wavelength.49

To study energy transfer mechanisms, it is useful to compare
both spectra (PL and OA) of Fig. 5, driving the attention to the
Förster mechanism that is particularly the most important pro-
cess that occurs at the nanometric scale.49 For an efficient energy
transfer via Förster mechanism there should be interaction
between transition dipoles of a donor and an acceptor to the spec-
tral overlap of donor emission and acceptor absorption. So, a
good overlap between the PL and OA curves would determine the
efficiency of the energy transfer. The spectra of Fig. 5 con-
firm that this behaviour may be stronger in PbSe dots than in PbS
dots. This is a reflection of a Stokes shift of about 5 times larger.

Figure 6 displays the PL spatial profile on the sample surface
measured at different emission energies from the PL of the PbS
nanocrystal QDs, at low temperature. The insert shows the
corresponding PL spectrum. Taking into account the circular
symmetry of the spatial profile around the laser spot, we just plot
the PL intensity profile starting from the centre of the laser spot
(set at 0 μm). It was noted that the spatial profiles depend strongly
on the detection energy. It is also found that as the detection
energy decreases the PL intensity decay becomes larger. On the
lowest detection energy the spatial decay can be as long as 200
μm (see curve "a" and the corresponding detection energy).

![Fig. 5. Room temperature PL (solid lines) and optical absorption (dotted lines) spectra from PbS (left side) and PbSe (right side) nano-
crystalline QDs.](image-url)
What is happening is that the PL spatial profile widens steadily with increasing dot size (lower energies), been indicative of energy flowing into larger dots. These energy (size) dependent profiles unambiguously show direct energy transfer from small dots to larger dots. We argue that indirect coupling between different sub-bands via photon reabsorption plays an important role.

**Figure 7** shows the results from similar measurements performed in Fig. 6, but for PbSe QDs. Our first comment is that the difference between the PL spatial profiles is smaller if compared to the PbS QDs. This behaviour is explained by using an argument the dispersion of quantum dot size in these two cases. From PL spectra, we find that the emission peak energy from PbS quantum dots is larger than that of PbSe QDs, using the same thermal treatment of the glass matrix. So, it implies that in our interesting range the sizes of PbS QDs are smaller compared to PbSe QDs. At the same time, the energy levels of a carrier in large QDs become less sensitive to the variation of QD size. Thus, it is expected that the difference between the PL spatial profiles becomes smaller, according to Fig. 7. However, in spite of small difference, the process of energy flow between different subsets of dots may also occur in PbSe dots in a reduced manner.

The fact that the PbSe sample has a small variation with temperature accounts for the small distance between the energy levels implying lower interaction with the phonons in the matrix.**

**Figure 8** displays the PL spatial profile on the sample surface obtained by detecting at the PL peak, at different temperatures. The samples were prepared with different annealing times of 3, 5 and 12 h. The thermal treatment clearly indicates that the QDs sizes increase as the annealing time increases. Thus, the PL peak position shifts to lower energies. Comparison between the data obtained from numerical calculation of the energy levels and the energy associated to the features observed in the optical absorption spectra can be used to estimate the PbS QD sizes. By doing this, the average PbS QD sizes for the 3, 5 and 12 h samples were estimated in 2.7, 4.0 and 9.0 nm, respectively. Remembering that the luminescence area on the surface is symmetrical around the laser excitation spot, the PL intensity profile is plotted from the centre of the laser spot located at 0 μm. By comparing the PL spatial profile for those samples, the 3 h sample clearly shows the widest profile, on the other hand, the 12 h sample shows the shortest profile. This picture demonstrates that the efficiency of energy transfer become higher for the sample with smaller QD size (3 h sample), and lower for the sample with the largest QD size (12 h sample).

The results demonstrate that the photon diffusion length that characterizes the PL spatial distribution is larger when we measure on the low-energy side of the PL spectrum. This behavior would account for the energy transfer between different subsets of dots. The subset of small dots that corresponds to the highest
emission energies works as a source of excitation for the subset of larger dots (lower energies). Moreover, photons that are emitted from the subset of small dot are strongly absorbed (by dots of same size or larger). On the other hand, photons that are emitted from the subset of large dots are only absorbed by the same subset. For this reason we would expect that the PL spatial distribution widens on the low-energy side of the PL spectrum.

It has been shown that efficient energy transfer occurs between quantum dots having a significant band gap energy difference, i.e., between dots of markedly different sizes. The measurements of the PbS dots indicate that due to the large Stoke shift reabsorption is less effective, and the energy transfer is more efficient between quantum dots having a significant band gap energy difference. For this reason, varying the energy gap of the dots we find different spatial PL profiles. On the other hand, when we measure the PbSe nanocrystal QDs reabsorption is comparatively more effective, and the energy transfer may occur between dots having the same band gap energy or small gap energy difference. Thus, this behaviour makes the PL profiles similar.

5. Conclusion

Compared to epitaxially grown techniques such as molecular beam epitaxy, semiconductor-doped glasses is low cost to fabricate. Because of their unique electronic and optical properties, semiconductor QDs found wide applications in the optoelectronics and optical communication. In photonsics, they find applications such as saturable absorbers. PbS and PbSe QDs are interesting for infra-red application due to their narrow band gap. In summary, it was presented a novel technique to study energy transfer mechanisms using semiconductor nanocrystal doped glasses. The results directly revealed the energy transfer from smaller to larger dots in nanocrystal QDs. Energy transfer between different sizes dots can be quite reduced when the reabsorption is significantly high. Based on these findings, further improvements in size selectivity will permit highly efficient energy flows in nanocrystal doped glasses.

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References

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Ilmo. Sr.

Fabiano de Souza Valentim
Chefe do Departamento de Avaliação

Referência: Projeto CEX 2154-06 Caracterização óptica de nanopartículas semicondutoras utilizando microluminescência resolvida espacialmente
Referência ao ofício DAV 1115/2009

Coordenador: Prof. Adamo Ferreira Gomes do Monte

Em anexo, encontram-se os comprovantes (cópias) dos trabalhos apresentados em congressos científicos e comprovantes das orientações de iniciação científica.

Agradecemos o apoio recebido e reiteramos nossos protestos de estima e consideração.

Atenciosamente,

Adam Ferreira Gomes do Monte
Certificamos que Adamo Ferreira Gomes do Monte apresentou como Co-autor(a) da Comunicação Oral intitulada "Investigação das propriedades de transporte de portadores em semicondutores usando a técnica da imagem da luminescência" na III Semana Acadêmica da Universidade Federal de Uberlândia, realizada pela Pró-Reitoria de Graduação, no período de 07 a 11 de agosto de 2006, no Campus Santa Mônica.

Uberlândia, 11 de agosto de 2006.

Profª Drª Vera Lúcia Puga
Pró-Reitora de Graduação
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Je soussignée, Myriam PERONNET Directrice de la Formation Continue,
I subsign, Myriam PERONNET, head of the service of continuing education,

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which took place: July 7-11, 2008 in Lyon (31 hours)

Fait à Villeurbanne, le 11 juillet 2008/
Made in Villeurbanne, Friday, July 11

Myriam PERONNET
O Comitê Organizador certifica que o trabalho SPATIAL ENERGY TRANSFER IN Nd3+DOPED GLASSES AS A FUNCTION OF CONCENTRATION de autoria de Adamo F. G. Monte, Elias O. Serqueira, Noellio O. Dantas foi apresentado na sessão PROPRIEDADES ESTRUTURAIS E DINÂMICAS DE MATERIAIS (Vidros, Amorfos e Materiais Desordenados) no XXIX Encontro Nacional de Física da Matéria Condensada realizado de 9 a 13 de Maio de 2006 em São Lourenço, MG, Brasil.

São Lourenço, 12 de Maio de 2006

[Assinatura]
Fernando Lázaro Freire Junior
Coordenador de Programa

XXIX ENCONTRO NACIONAL DE FÍSICA DA MATÉRIA CONDENSADA

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- Executar o plano de pesquisa aprovado pelo Comitê Científico do Programa.
- Não manter vínculo empregatício de qualquer natureza, ou de estágio remunerado ou não, e dedicar-se integralmente às atividades acadêmicas e de pesquisa, em pelo menos 20 horas semanais, sob orientação do pesquisador responsável.
- Estar recebendo apenas esta modalidade de bolsa, vedada qualquer outra acumulação.
- Participar de todos os eventos promovidos pelo Programa.
• Encaminhar à Diretoria de Pesquisa fichas trimestrais, conforme o calendário, Relatório Técnico Parcial e Relatório Técnico-Científico Final (no formato de um artigo a ser publicado em revista).
• Apresentar os resultados alcançados sob a forma de posters ou exposições orais, por ocasião dos Seminários de Iniciação Científica.
• Obedecer às demais exigências contidas no Edital de seleção publicado.

<table>
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<th>CALENDÁRIO DE ENTREGA</th>
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<tr>
<td><strong>Fichas Trimestrais</strong></td>
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<tr>
<td>30 de maio de 2008</td>
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<td>05 de dezembro de 2008</td>
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**DEVERES DO ORIENTADOR**

• Orientar e avaliar o bolsista em todas as fases do seu Programa de trabalho; incluindo elaboração de relatório Técnico-Científico Final (no formato de um artigo a ser publicado em revista) e de outros meios para divulgação dos resultados.
• Repassar aos bolsistas todas as informações recebidas referentes ao Programa.
• Encaminhar à Diretoria de Pesquisa eventuais alterações do Plano de pesquisa, com uma antecedência mínima de 130 dias do término da bolsa.
• Assegurar condições e acesso às instalações laboratoriais imprescindíveis à realização do plano de pesquisa do bolsista.
• Acompanhar na medida do possível, as exposições dos trabalhos realizados pelos bolsistas em Congressos, Seminários e, principalmente por ocasião do Seminário de Iniciação Científica.
• Incluir o nome dos bolsistas de Iniciação Científica nas publicações e nos trabalhos apresentados em Congressos e Seminários, para cujos resultados houve a participação efetiva dos mesmos.
• Prestar consultoria “ad hoc”, emitindo pareceres técnicos na análise de relatórios dos bolsistas, quando solicitados pela DIRPE e ou CNPq.

**DISPOSIÇÕES FINAIS**

• O uso do numerário recebido a título de bolsa, definida no primeiro parágrafo, do presente termo de concessão, é de uso livre e exclusivo do bolsista, sendo vedada sua administração ou utilização por parte do Orientador.
• A Pró-Reitoria de Pesquisa e Pós-Graduação, ouvido o Comitê Assessor do Programa, poderá susporre a concessão da Bolsa, nos casos de não cumprimento deste Termo. Casos excepcionais serão julgados pela Comissão de Iniciação Científica da UFU.

Uberlândia, 15 de janeiro de 2008.

[Assinaturas]

Orientador

Bolsista
Termo de Concessão de Bolsa Institucional de Iniciação Científica

Prof. (a) Orientador (a): Adamo Ferreira Gomes do Monte

Unidade Acadêmica: INFIS

Aluno (a) Bolsista: Kelly de Souza Fernandes

Projeto nº.: A-010/2006

Pelo presente termo, a Pró-Reitoria de Pesquisa e Pós-Graduação da Universidade Federal de Uberlândia, por meio do Programa Institucional de Bolsas de Iniciação Científica, doravante designada PIBIC/CNPq/UFU, concede ao professor e aluno acima referidos participação no Programa Institucional de Iniciação Científica, por meio de (1) uma bolsa com a duração de 12 meses (agosto de 2006 a julho de 2007), sob o compromisso de concordância com a filosofia e objetivos do Programa.

FILOSOFIA

O PIBIC tem como princípios despertar vocações científicas e talentos potenciais entre os alunos dos cursos de graduação, possibilitando a aprendizagem de técnicas e métodos norteados para a produção crítica do conhecimento.

OBJETIVOS DO PROGRAMA

- Estimular pesquisadores produtivos a engajar estudantes de graduação no processo acadêmico, otimizando sua capacidade de orientação à pesquisa na instituição.
- Despertar vocação científica e incentivar talentos potenciais entre estudantes de graduação, mediante suas participações em projetos de pesquisa.
- Proporcionar aos bolsistas a aprendizagem de métodos e técnicas científicos, estimular o desenvolvimento da criatividade intelectual, bem como o engajamento crítico e responsável na sociedade, como decorrência das condições criadas pelo confronto direto com os problemas de pesquisa.
- Qualificar candidatos para os programas de pós-graduação e aprimorar o processo de formação de cidadãos ativos por meio da formação profissional.

DEVERES DO BOLSISTA

- Executar o plano de pesquisa aprovado pelo Comitê Científico do Programa.
- Não manter vínculo empregatício de qualquer natureza, estágio remunerado ou não.
- Receber apenas esta modalidade de bolsa, vedada qualquer outra acumulação.
- Dedicar-se integralmente as atividades acadêmicas e pelo menos 20 horas semanais ao plano de trabalho, sob orientação do pesquisador responsável.
- Participar de todos os eventos promovidos pelo Programa.
• Encaminhar à Diretoria de Pesquisa fichas trimestrais, conforme o calendário. Relatório Técnico Parcial e Relatório Técnico-Científico Final, no formato de um artigo a ser publicado em revista.
• Apresentar os resultados alcançados sob a forma de posters ou exposições orais, por ocasião dos Seminários de Iniciação Científica.
• Obedecer às demais exigências contidas no edital de seleção publicado.

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<th>Calendário De Entrega</th>
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<tr>
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<td>31/10/2006</td>
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<td>02/05/2007</td>
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</tbody>
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DEVERES DO ORIENTADOR

• Orientar e avaliar o bolsista em todas as fases do seu plano de trabalho, incluindo a elaboração do Relatório Técnico-Científico Final, no formato de um artigo a ser publicado em revista e outros meios de divulgação dos resultados.
• Repassar aos bolsistas todas as informações referentes ao Programa.
• Encaminhar à Diretoria de Pesquisa eventuais alterações do plano de trabalho do aluno, com uma antecedência mínima de 130 dias do término da bolsa.
• Assegurar ao bolsista as condições de acesso às instalações laboratoriais e demais condições imprescindíveis à realização do plano de trabalho.
• Acompanhar as exposições dos trabalhos realizados pelos bolsistas em Congressos, Seminários, principalmente por ocasião do Seminário de Iniciação Científica/UFU.
• Incluir o nome do bolsista de Iniciação Científica nas publicações e nos trabalhos apresentados em Congressos e Seminários em que houve a participação efetiva do mesmo.
• Prestar consultoria “ad hoc”, emitindo pareceres técnicos na análise de relatórios dos bolsistas, quando solicitados pela DIRPE e ou CNPq.

DISPOSIÇÕES FINAIS

• O uso do numerário recebido a título de bolsa, definido no primeiro parágrafo do presente termo de concessão, é de uso livre e exclusivo do bolsista, sendo vedada sua administração ou utilização por parte do Orientador.
• A Pró-Reitoria de Pesquisa e Pós-Graduação, assessorada pela Comissão de Iniciação Científica, poderá suspender a concessão da bolsa nos casos de não cumprimento deste Termo. Outros casos excepcionais serão avaliados pela mesma Comissão, para emissão de pareceres ao Coordenador Institucional do Programa e ao Pró-Reitor de Pesquisa e Pós-Graduação.

Uberlândia, 20 de julho de 2006.

[Assinaturas]

Orientador

Bolsista
Certificate of Presentation

This letter is to certify that Dr. A. F. G. Monte presented the paper entitled “Carrier transport investigation in short-wavelength InAs/AlGaAs quantum dots” at the “2nd International Conference on Surfaces, Coatings and Nanostructured Materials – NanoSMat2007”, which has been held from 9 to 11 July 2007, in Portugal.

Prof. Dr. Nasar Ali
NanoSMat 2007 – Chairman / Contact: nasar@nanoismat.org

WEBPAGE: www.nanoismat.org
11th of July 2007

Certificate of Presentation

This letter is to certify that Dr. A. F. G. Monte presented the paper entitled “Optical characterization of CdS nanoparticles embedded in polymeric spherical microspheres” at the “2nd International Conference on Surfaces, Coatings and Nanostructured Materials – NanoSMat2007”, which has been held from 9 to 11 July 2007, in Portugal.

Prof. Dr. Nasar Ali

NanoSMat 2007 – Chairman / Contact: contact@nanosmat.org WEBPAGE: www.nanosmat.org
11th of July 2007

Certificate of Participation

This letter is to certify that Dr. A. F. G. Monte attended the “2nd International Conference on Surfaces, Coatings and Nanostructured Materials – NanoSMat2007”, which has been held from 9 to 11 July 2007, in Portugal.

Prof. Dr. Nasar Ali
NanoSMat 2007 – Chairman / Contact: contact@nanosmat.org WEBPAGE: www.nanosmat.org
O Comitê Organizador certifica que ADAMO FERREIRA GOMES DO MONTE participou do XXIX Encontro Nacional de Física da Matéria Condensada realizado de 9 a 13 de Maio de 2006 em São Lourenço, MG, Brasil.

São Lourenço, 13 de Maio de 2006.

Marcia C. B. Barbosa
Coordenadora Geral

XXIX ENCONTRO NACIONAL DE FÍSICA DA MATÉRIA CONDENSADA

CERTIFICADO

REALIZAÇÃO:

SOCIEDADE BRASILEIRA DE FÍSICA
Certificate of Participation

I hereby acknowledge that A. F. G. Monte attended the conference and presented the work entitled
“Nonlinear effects of the photocurrent in self-assembled InAs/GaAs quantum dots”


Prof. Dr. Gil de Aquino Farias
ICSNN 2008 Chairman
Certificate of Participation

I hereby acknowledge that A. F. G. Monte attended the conference and presented the work entitled

“Electric field effects on the carrier migration in self-assembled InAs/GaAs quantum dots”


Prof. Dr. Gil de Aquino Farias
ICSNN 2008 Chairman
13th Bразиліан Workshop on Semiconductor Physics
APRIL 1-5, 2007 - SÃO PAULO, SP, BRAZIL

CERTIFICATE

We hereby certify that the work

Photocurrent investigations in self-assembled quantum dots by Adanom F.G. Monte, Fan yao Qu, José Melo Junior, José R.K.F. Santos, M. Hopkinson

has been presented in the 13th Brazilian Workshop on Semiconductor Physics, held in São Paulo, SP, Brazil, April 1-5, 2007.

São Paulo, April 5, 2007

Antônio José Roque da Silva
Chair

Lucy Vitória Credidio Assali
Secretary

Márcia Carvalho de Abreu Fantini
Secretary
CERTIFICATE

We hereby certify that

ADAMO FERREIRA GOMES DO MONTE

attended the 13th Brazilian Workshop on Semiconductor Physics, held in São Paulo, SP, Brazil, April 1-5, 2007.

São Paulo, April 5, 2007

Antônio José Roque da Silva  Lucy Vitória Credidio Assali  Márcia C. de Abreu Fantini
Chair  Secretary  Secretary

Signatures
O Comitê Organizador certifica que ADAMO FERREIRA GOMES DO MONTE participou do XXXI Encontro Nacional de Física da Matéria Condensada realizado de 5 a 9 de Maio de 2008 em Águas de Lindóia, SP, Brasil.

Águas de Lindóia, 9 de Maio de 2008.

Airton Abravanel Martins
Coordenador Geral

Marcelo Leite Lyra
Coordenador de Programa
O Comitê Científico certifica que o trabalho Anomalous photocurrent in a self-assembled quantum dot de autoria de Adamo F. G. do Monte, Qu Fanyao, Flávio A. M. Marques, Mark Hopkinson foi apresentado na sessão SEMICONDUTORES (Heteroestruturas, poços quânticos, super-redes, pontos quânticos) no XXXI Encontro Nacional de Física da Matéria Condensada realizado de 5 a 9 de Maio de 2008 em Águas de Lindóia, SP, Brasil.

Águas de Lindóia, 8 de Maio de 2008
O Comitê Científico certifica que o trabalho **Optical properties of polystyrene doped with acai oil and β-carotene** de autoria de Nizamara S. Pereira, Adano F. G. do Monte, Djalmir N. Messias, Maria José A. Sales, Paulo César de Morais foi apresentado na sessão **SEMICONDUTORES (Dispositivos orgânicos e inorgânicos, sistemas moleculares, transporte em nanoestruturas)** no XXXI Encontro Nacional de Física da Matéria Condensada realizado de 5 a 9 de Maio de 2008 em Águas de Lindóia, SP, Brasil.

Águas de Lindóia, 8 de Maio de 2008

[Signatures]
O Comitê Científico certifica que o trabalho *Thermal optical properties determination by microluminescence and optical thermometry techniques* de autoria de Djalmir N. Messias, Adamo F. G. do Monte, Omar O. D. Neto foi apresentado na sessão PROPRIEDADES ESTRUTURAIS E DINÂMICAS DE MATERIAIS (Teoria e Modelagem) no XXXI Encontro Nacional de Física da Matéria Condensada realizado de 5 a 9 de Maio de 2008 em Águas de Lindóia, SP, Brasil.

Águas de Lindóia, 8 de Maio de 2008
Certificamos que ÁDAMO FERREIRA GOMES DO MONTE freqüentou o mini-curso “NANOTECNOLOGIA APLICADA A SENSORES”, com duração de 08 (oito) horas, como atividade do I Simpósio Nacional de Nanotecnologia e Nanomedicina – I NanoMed, realizado pelo Instituto de Genética e Bioquímica e Instituto de Química da Universidade Federal de Uberlândia, no dia 26 de Julho de 2007.


Luiz Ricardo Goulart Filho  
Comissão Organizadora

João Marcos Madurro  
Comissão Organizadora
O Comitê Organizador certifica que ADAMO FERREIRA GOMES DO MONTE participou do XXX Encontro Nacional de Física da Matéria Condensada realizado de 7 a 11 de Maio de 2007 em São Lourenço, MG, Brasil.

São Lourenço, 11 de Maio de 2007.
Certificamos que ÁDAMO FERREIRA GOMES DO MONTE participou do I Simpósio Nacional de Nanotecnologia e Nanomedicina – I NanoMed, realizado pelo Instituto de Genética e Bioquímica e Instituto de Química da Universidade Federal de Uberlândia, no dia 27 de Julho de 2007, com atividades que perfizeram um total de 08 horas.


Luiz Ricardo Goulart Filho
Comissão Organizadora

João Marcos Madurro
Comissão Organizadora