Effects of size restriction on donor-acceptor recombination in AgBr

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The behavior of donor-acceptor (DA) recombination luminescence in quantum confined AgBr has been investigated. The DA luminescence decay, after pulsed excitation, became longer lived as the nanocluster size decreased. This result differs from theoretical expectations and from observations with AgI nanoclusters. The DA lifetime increase with decreasing size is due to an increase in yield and lifetime of ''free'' excitons that slowly dissociate into ''close'' donor-acceptor pairs, giving rise to an ''exciton dribbling'' effect.

I. INTRODUCTION

With both donors and acceptors present in a semiconductor, Coulomb interactions between them modify the energies in such a way that the recombination energy is distance-dependent.[1,2] Distant donor-acceptor pairs result when the separation r between the acceptor and donor ions is much greater than the internal dimensions (the Bohr radii) of either the neutral acceptor or neutral donor. Close donor-acceptor pairs result when r is comparable to or smaller than the dimensions of either the donor or acceptor. The recombination energy of a distant donor-acceptor pair is given by

$$E_{\mathrm{DA}} = E_g - (E_D + E_A) + e^2/\varepsilon r, \tag{1}$$

where E_g is the band-gap energy, E_D and E_A are the binding energies of the donor and acceptor, and the last term is the Coulomb interaction of the donor-acceptor pair separated by r, where e is the charge on an electron and ε is the static dielectric constant.

Recombination is a tunneling-assisted process for distant pairs and a more complex process for close pairs. For substitutional impurities, discrete lines are observed in photoluminescence of a number of semiconductors.[1–3] As r increases, the emission lines merge to form a broad band. Sharp lines in emission spectra are observed only in semiconductors where the electron-phonon coupling is weak, which is not the case for silver halides. Recombination between near pairs is more probable than between distant pairs, which leads to the recombination luminescence shifting to longer wavelengths with time after pulsed excitation. This dynamic phenomenon was first quantitatively modeled by Hopfield *et al.*[1] Later Thomas *et al.*[4] detailed a quantitative model for the kinetics of radiative recombination of randomly distributed donors and acceptors in an attempt to account for the long and nonexponential decay curves of the emission observed after pulse excitation.

The broadband emission that occurs at low temperatures (4 K), ~2.48 eV (500 nm) in AgCl and ~2.14 eV (580 nm) in AgBr, both indirect-gap semiconductors, has been characterized as donor-acceptor recombination.[5] Recent investigation of AgI has also shown that its broad emission peaking at 3.1 eV (450 nm) is also due to donor-acceptor recombination.[6,7] Studies of the low-temperature excitation spectra of various AgBr samples have shown that, when monitoring either the iodide bound exciton (IBE) emission at 500 nm or the donor-acceptor recombination at 580 nm, the exciton excitation spectrum is observed below the band edge. This indicated that ''free'' excitons were trapped at both impurity iodide to form IBE and at close donor-acceptor pairs that subsequently radiatively recombined.[8] Optically detected magnetic resonance (ODMR) spectra of AgBr have demonstrated that the donor-acceptor emission has contributions from both distant and close pairs.[9]

Size restriction and DA pair recombination

Quantum confinement occurs when the spatial extent of a material (boundary conditions) begins to affect the eigenenergies of the electronic wave function, causing the electronic properties to differ from those of bulk materials. Quantum confinement effects become noticeable when the size of the material is the same order of magnitude as the bulk exciton Bohr radius. At this point, the band gap begins to blueshift. The blueshift can be described conceptually by a particle in a box.[10,11] Size restriction can also exclude impurities and defects from materials. In AgBr nanocrystals, free-exciton luminescence dominates the normally intense impurity iodide bound exciton (IBE) emission.[12] The IBE emission becomes essentially undetectable when, for a given impurity concentration, only one nanocrystal in 100 contains an impurity iodide ion.

Size restriction will limit the maximum separation of DA pairs. Thus, pair recombination in a confined system should have a limited luminescence peak redshift for long delay times following pulsed excitation. Considering the total light intensity decay kinetics, the loss of long-lived radiative de-

cay components would be expected in the nanocrystals. The limited extent of the nanocrystals ensures that only the transitions with higher probabilities occur, i.e., those between close DA pairs. This assumes that the trapped carriers are not decaying through other channels and that more donor-bound electrons and acceptor-bound holes are not being created after the initial excitation. Recent work on AgI nanocrystals has shown that the luminescence decay after pulsed excitation is truncated as the nanocluster size is decreased.[6,7]

II. EXPERIMENT

Microcrystals of AgBr were prepared as gelatin-stabilized crystallites. In a typical preparation, 15 g of gelatin (collagen) was dissolved in 200 mL of water in a stainless-steel mixing container fitted with a mechanical stirrer. Next, 100 mL each of aqueous 2 M $AgNO_3$ and 2 M NaBr were added to the gelatin mixture in a double jet with rapid stirring. Typical preparation temperature ranged from 35 to 45 °C with lower temperatures yielding smaller crystals. A sample with crystallites having a mean diameter of 41 nm was prepared at 35 °C.

AgBr nanocrystals were synthesized in aqueous media. A typical preparation followed a synthesis detailed elsewhere[13] in which small amounts of silver salts and halide were injected into a solvent containing a size-restricting polymer. 90 mL of 0.01 M $AgNO_3$ and 100 mL of 0.01 M NaBr at 10 °C were injected into 10 mL of H_2O (20 °C) with 1.0 wt. % low-molecular weight poly(vinyl alcohol) (PVA, molecular weight ~8–12 k) and were mixed with a magnetic stir bar for 1 min in a 20-mL beaker under red light conditions. The beaker was then put into a 10 °C bath until the samples were ready to be introduced into the cryostat. An additional size restriction agent, sodium polyphosphate, was also used in some preparations because of its reported efficacy in aqueous preparation of colloidal quantum dots.[14]

Two specific samples with diameters of 41 ± 7 and 8 ± 1.7 nm, respectively, are detailed below although the effects discussed were found in all samples studied. Transmission electron microscopy (TEM) was used to determine the size and morphology of most of the samples. However, the sizes of some of the nanocrystal samples were calculated from the blueshift of the exciton luminescence peak. Previous studies have correlated the blueshift in exciton emission from AgBr nanocrystals produced by reverse micelles with the crystallite size measured by TEM.[15] The distribution width (error in size) is taken as the full width at half maximum (FWHM).

Low-temperature, steady-state photoluminescence (PL) spectra were obtained using a system described elsewhere.[9] An acousto-optic modulator (AOM), argon, ion laser and gated photon-counting system was used to measure the emission decay from the 41-nm sample while an N_2 pulsed laser system, described in Ref. 5, was used to measure the lifetimes of the 8-nm sample because of lower levels of emission.

III. RESULTS AND DISCUSSION

The low-temperature luminescence spectra from different sized AgBr crystals are shown in Fig. 1. The spectra are consistent with previously reported data.[16] In both the bulk and 41-nm samples, emission from free and weakly bound excitons is observed as a narrow line structure at about 2.68 eV. In the 8-nm nanocrystal sample, the free-exciton luminescence is blueshifted by 30 meV and all structure is lost. The broadbands with maxima around 2.1 and 2.5 eV originate from donor-acceptor pair recombination and iodide-bound exciton luminescence, respectively. Emission from DA pair recombination is evident in all samples. The effects of size restriction on the DA recombination dynamics have remained unexplored except for some preliminary work.[16] Results from the time-resolved experiments are plotted in Fig. 2. Three nanocrystalline samples with mean diameters ranging from 7.5 to 10.5 nm were examined along with the 8-nm preparation shown. All had nearly identical decay curves over the dynamic range plotted.

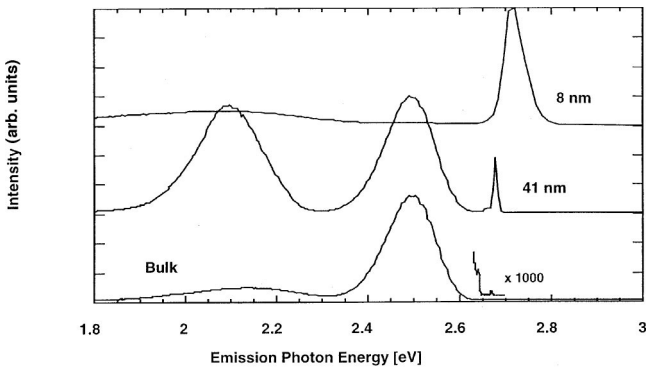

FIG. 1. Steady-state photoluminescence from a bulk (3×3 mm) crystal of AgBr, gelatin prepared AgBr nanocrystals (41 nm), and PVA size-restricted AgBr nanocrystals (8 nm). $E_L = 3.81$ eV, broad survey resolution is 4 meV, high resolution is 1 meV. $T = 6$ K. Free-exciton luminescence is found at 2.68 eV, the iodide-bound exciton luminescence at 2.5 eV, and the donor-acceptor recombination centered around 2.1 eV.

The decay of the emission from the 41-nm sample compares well with data on bulk AgBr.[5] Previous investigators[5] were able to fit the light decay data over three orders of magnitude using the theoretical model outlined in Ref. 4.

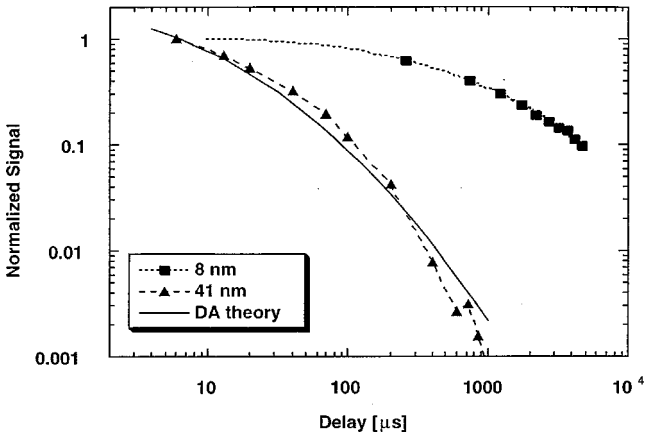

FIG. 2. Comparison of DA pair recombination dynamics in samples with 41- and 8-nm crystals. The solid line is a theoretical DA decay profile for $N_D > N_A$, $N_D = 10^{18}\,\mathrm{cm}^{-3}$, $W_{\max} = 10^6\,\mathrm{s}^{-1}$, and $R_d = 12$ Å. The 8-nm sample was excited at $E_L = 3.68$ eV and the recombination detected at $E_S = 2.066 \pm 0.0013$ eV, while $E_L = 3.53$ eV and $E_s = 2.084 \pm 0.0014$ eV for the 41-nm sample. $T = 6$ K.

They used a majority impurity concentration of $10^{18}\,\mathrm{cm}^{-3}$. In Fig. 2, the theoretical DA decay profile is plotted with the following parameters for the majority impurity concentration, the radiative rate, and the critical distance, respectively: $N_D = 10^{18}\,\mathrm{cm}^{-3}$, $W_{\max} = 10^6\,\mathrm{s}^{-1}$, and $R_d = 12\,\text{Å}$. A small increase (much less than an order of magnitude) in N_D would increase the curvature of the theoretical plot and fit the data better. But, $10^{18}\,\mathrm{cm}^{-3}$ appears to be the correct order of magnitude for the majority impurity concentration.

As is evident from Fig. 2, the decay of the luminescence from DA pair recombination in the 8-nm preparation is much slower than the decay from the larger crystal. This behavior is quite unexpected. As indicated above, the luminescence decay rate was expected to increase because the limited spatial extent of the nanocrystal should force the wave functions of the carriers bound to the DA pairs closer than they would otherwise be in the bulk or microcrystals. And indeed, the expected behavior was observed in AgI nanocrystals.[6,7] The transition rate should increase with the proximity of the wave functions of the donor-bound electron and the acceptor-bound hole. Since the observed behavior of the recombination rate clearly diverges from what was expected, some of the assumptions for normal DA recombination must not be valid for AgBr nanocrystals. Originally, it was assumed that after initial excitation there was no other source creating DA pairs. DA pair creation after the excitation pulse could explain the data presented above.

The lifetime increase observed in the free-exciton emission with decreasing crystal size was reported to be due to impurity exclusion and the decreasing importance of surface annihilation of excitons.[8] The former results in shutting off the iodide-bound exciton recombination luminescence, a competitive radiative pathway with a much higher decay rate. The latter results in the loss of a competitive nonradiative pathway. The former is a well-documented phenomenon of nanocrystals. As for the latter, investigators in Ref. 8 suggested three possible reasons for the decreasing importance of surface annihilation of free excitons: surface reconstruction, Coulomb interaction restricting holes to the interior of the crystal, and a decrease in LO-phonon scattering rate resulting from a change in exciton-phonon interaction. These investigators also determined that free excitons were trapped to form both iodide-bound excitons and ''close'' DA pairs that gave rise to DA emission. This suggests that the long-lived free excitons in AgBr nanocrystals are dissociating into donor-acceptor pairs, which are then subsequently recombining to give the appearance of $a \sim 1$ ms decay. If this were the case, it would be expected that the exciton lifetime and DA recombination time would be similar in nanocrystals.

The exciton emission lifetimes were measured for both the 41-nm and the 8-nm samples. Both free-exciton (FE) and an impurity bound exciton (BX_8) emission were observed in the 41-nm sample. The FE and BX_8 excitons had first-order lifetimes of 15.8 and 19.1 μs, respectively. These lifetimes are shorter than the $1/e$ time for the DA emission, which is 40–50 μs. The exciton emission from the 8-nm sample was decomposed into two first-order decays with $\tau_1 = 185\,\mu$s and $\tau_2 = 611\,\mu$s. The $1/e$ time for the DA decay from the 8-nm sample was found to be $\approx 700\,\mu$s. Thus, the extended DA recombination time observed in AgBr nanocrystals has a $1/e$ time comfortably close to the longer first-order decay of the exciton emission.

IV. CONCLUSIONS

The effects of size restriction on the DA recombination dynamics in nanocrystalline AgBr have been explored. The lifetime of the DA recombination was found to be extended as size decreased, a result diverging from theoretical expectations and observations of DA recombination dynamics in AgI nanocrystals. Previous workers had shown that quantum confinement increased the lifetime of free excitons in AgBr and that these free excitons dissociate into ''close'' DA pairs. An exciton lifetime increase from approximately 20 to 600 μs with decreasing cluster size was observed here. It is the dissociation of these longer-lived excitons into DA pairs or ''exciton dribbling'' that extends the lifetime of the DA recombination in AgBr nanocrystals.

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