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Citation: Applied Physics Letters **67**, 653 (1995); doi: 10.1063/1.115192 View online: http://dx.doi.org/10.1063/1.115192 View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/67/5?ver=pdfcov Published by the AIP Publishing

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Linear and nonlinear transmission of Cu_xS quantum dots

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(Received 28 March 1995; accepted for publication 16 May 1995)

Cu_xS nanocrystals (NC's) are reported. The samples are prepared by a CdS-to-Cu_xS chemical conversion from the glasses originally containing CdS NC's. A room-temperature linear absorption of the converted samples shows several well resolved peaks with spectral positions from red to blue. These spectral features are explained by size quantization within Cu_xS NC's (~4 nm radius) with different copper deficiency [x is in the range from 1.8 (digenite) to 2 (chalcosite)]. A strong bleaching of the samples with a 3-ns relaxation is observed in the pump–probe measurements. A high value of the third-order nonlinear susceptibility (~10⁻⁷ esu) is derived from the nonlinear transmission spectra. © 1995 American Institute of Physics.

Semiconductor nanocrystals (NC's) grown in a glass matrix^{1,2} or prepared as colloids³ are often referred to as quasi-zero-dimensional systems or quantum dots. The energy spectrum of NC's and in particular the position of the lowest optical transition (the energy band gap in a quantum dot), can be varied in a broad range by changing the average NC size. Strong and fast optical nonlinearities^{4,5} as well as optical gain and lasing⁶ reported for these materials make them attractive for potential applications in optoelectronics and signal processing.

A great amount of the experimental and theoretical work has been done on CdS, CdSe, and $CdS_xSe_{1-x} NC's^7$ (in what follows we will refer to the NC's of these types by using a general notation: CdSSe NC's). New methods of preparation are developed to synthesize the CdSSe NC's with a very sharp size distribution.^{8,9} It looks attractive to combine a developed technology of the CdSSe-doped glasses with methods of a chemical conversion to prepare NC's of new compositions.

In the present letter we report on $Cu_x S NC$'s prepared by a chemical conversion from glasses containing CdS quantum dots. The discrete features recorded in linear absorption of the converted samples clearly indicate the effect of size quantization within $Cu_x S NC$'s with different copper deficiencies. A change in the copper amount from x=2 (chalcosite) to x=1.8 (digenite) leads to a strong high-energy shift of the lowest optical transition by about 0.54 eV. Nonlinear transmission studies show a strong enhancement of the thirdorder nonlinearity (by 2–3 orders of magnitude) in comparison with that in CdSSe quantum dots.

The studies of $Cu_x S$ semiconductor compounds have mainly been carried out in the context of a $Cu_x S/CdS$ -solar-cell operation.¹⁰ The most common method of producing copper sulfides is by a topochemical reaction from CdS single crystals.^{11,12} The copper sulfide crystals with different copper deficiencies [$Cu_{1.96}S$ (djurleite), $Cu_{1.9}S$, $Cu_{1.8}S$ (digenite)] can be obtained successively by controlled oxidation of chalcosite (Cu_2S) .¹² We have used the conversion of CdS to Cu_xS to produce copper sulfide NC's in the glass matrix originally containing CdS NC's.

The source glass samples containing CdS NC's (~4 nm radius) are prepared by the usual technique of a secondary heat treatment.^{1,2} These samples are initially subjected to the electrostimulated ion exchange in a melt of the KNO₃ salt.¹³ The potassium ions introduced in the glass matrix by this procedure mediate the ion exchange at the second stage of the preparation when the samples are treated in a melt of the $CuSO_4$ salt (for details see Ref. 14). The two-stage procedure applied results in the formation of a thin surface layer (d=40–50 μ m) with a definite color change. In contrast to the yellow color of the source samples, the converted layer is colored nonuniformly from red to brown. This transformation can be explained in terms of a two-step ion exchange: The copper ions first substitute for the potassium ions in the glass matrix and then for the cadmium ions in the CdS NC's leading to the formation of Cu_xS .

Figure 1 shows room-temperature absorption spectra of the three different regions of the converted layer colored dark-brown (a), brown (b), and red (c). For comparison, the absorption spectrum of a source CdS-doped glass is also shown. The absorption edge in the converted layer is red shifted from that in the source glass by more than 1 eV for the dark-brown region. The striking feature of the recorded spectra is a well resolved discrete structure which is not pronounced in the spectra of either the source glass or the bulk $Cu_x S$ crystals.¹² In the spectra shown in Figs. 1(a)-1(c), one can clearly resolve from two to four peaks. The positions of the peaks remain the same for the different regions of the sample but the number and the amplitudes of the peaks alter. Comparison of the spectra in Figs. 1(a) and 1(b) shows that the low-energy peak consists of the two bands which overlap. Finally, the analysis of the spectra allow us to identify five optical transitions (ω_{1-5}) with spectral positions 1.62, 1.834, 2.156, 2.586, and 2.684 eV.



FIG. 1. Linear absorption spectra of the converted layer (solid lines) and the source CdS-doped glass (dashed line). The spectra taken for the dark-brown, brown, and red regions of the converted layer are denoted as (a), (b), and (c), respectively.

The discrete structure of the absorption spectra clearly indicates a size quantization in the nanostructures formed in the converted layer. Given the preparation procedure the formation of the nanostructures of the two types could be expected: two-component CdS/Cu_xS heteronanoparticles (analogous to CdS/HgS NC's reported previously in Ref. 14) or/and one-component CuxS nanoparticles. However, the changes in the absorption spectra observed (see Fig. 1) cannot be explained by the formation of the heteroparticles. If the latter would be the case, the variations in the NC fraction converted to Cu_xS would lead to the continuous variations in the positions of the absorption bands that is not observed experimentally. This, as well as the analysis of the absorption spectra given below, is evidence for the nanostructures of the second type, namely, for the one-component $Cu_x S$ NC's. The nonuniformity of the converted layer will be shown to be explained by the presence of the NC's formed by the different copper sulfide phases.

The spectroscopic studies show that Cu₂S is an indirect gap semiconductor with a band-gap energy of ~1.2 eV.^{16,17} With increasing copper deficiency the energy band gap increases up to ~400 meV for digenite (x=1.8).¹² As suggested in Ref. 11, the phase transformation leads to the changes in the valence band structure, whereas the central minimum of a conduction band involved in both direct and indirect transitions remains unaffected. In the strong-confinement limit¹⁸ expected for the NC sizes under investi-

gation, the positions of the optically allowed transitions are determined basically by an electron effective mass. This leads to the conclusion that the confinement-induced shift of the lowest optical transition is independent of the copper deficiency and the type (direct/indirect) of the gap involved.

It is natural to assign the lowest band ω_1 in Fig. 1(a) to the transition, coupling the ground *s* electron and hole states in the NC's formed by Cu_xS with x=2, which corresponds to the lowest bulk band-gap energy. Peak ω_5 can be attributed to the same copper sulfide phase because it vanishes synchronously with peak ω_1 , going from region (a) to region (b) of the sample. The $\omega_5-\omega_1$ spacing (1.04 eV) is close to the separation between direct and indirect band gaps in bulk Cu₂S (~1 eV).^{19,20} This allows the assignment of the ω_5 band to the lowest transition originating from the direct gap in chalcosite. The direct transition is expected to lead to stronger absorption than the indirect one, which is consistent with data in Fig. 1(a).

The separation between ω_1 and ω_2 bands (~210 meV) is close to the difference in the band-gap energies (~200 meV)¹² in the bulk phases with x=2 and 1.9. Thus, the ω_2 band can be assigned to the lowest transition in the NC's with x=1.9. The intermediate phase with x=1.96 is not resolved in the spectra in Fig. 1, probably due to small energy separation (~30 meV)¹² between band gaps in chalcosite and djurleite.

The intense peak at ω_3 dominating the spectra in Figs. 1(b) and 1(c) can be attributed to the lowest transition in the Cu_xS NC's with x=1.8. This phase exhibits a direct band gap¹² that is consistent with a large magnitude of the ω_3 absorption. The energy separation between the ω_1 and ω_3 bands (540 meV) is somewhat larger than the shift between the absorption edges measured in the bulk phases with x=2and 1.8 (~400 meV).¹² This discrepancy probably arises from the existing uncertainty in the band parameters of the copper sulfides, as will be discussed below. Peak ω_4 observed along with peak ω_3 in Fig. 1(c) can be attributed to the second intense transition, coupling the lowest p states in the NC's of the same phase. In the CdSe NCs,²¹ the shift of this transition with respect to the bulk band-gap energy is about twice as large as the confinement-induced shift of the lowest transition. This is consistent with spectral positions of the ω_3 and ω_4 bands.

Summarizing the data on the linear absorption, we can conclude that region (c) of the converted layer is composed basically of the digenite NC's (x=1.8) with negligible contributions from the NC's in the other copper sulfide phases. Region (b) is formed mainly by the Cu_xS NC's with x=1.8 and 1.9; and the (a) region of the converted layer is a mixture of the NC's of all types including, probably, those in the unresolved x=1.96 phase.

The band-structure parameters of different copper sulfides have still been a matter of controversy. Among the other reasons, the discrepancy in the literature data can arise from the uncertainty in the composition of the bulk samples which is difficult to control at the preparation stage. The NC structures reported in the present paper have the advantage that different copper sulfide phases are clearly marked in the linear absorption by well resolved peaks. This provides a

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FIG. 2. DTS taken for the (c) region of the converted layer at different delay times after excitation. Inset shows the relaxation dynamic of the integral absorption changes.

way to improve the existing data on the band structure and to find, among other things, the electron mass m_e which has still been not well defined in literature. Comparing the confinement energies in the source and the converted samples one can easily get $m_e \approx 0.06 \ m_0 \ (m_0$ is a free electron mass). This value is much smaller than the electron mass in CdS (0.185 m_0) which explains a much more pronounced structure of the optical transitions in the Cu_xS NC's than in the source samples.

The CdSSe NC's are known to exhibit fast and fairly large optical nonlinearities. Room-temperature values of a third order nonlinear susceptibility $\chi^{(3)}$ are usually in the order of $10^{-9}-10^{-10}$ esu; and the nonlinearity relaxation times are typically of some tens of ps.^{5,22} To examine the nonlinear optical properties of Cu_xS NC's we have performed the measurements of the time-resolved nonlinear transmission by using a standard picosecond pump and probe technique with the 20-ps time resolution.

Time-resolved differential transmission spectra (DTS) measured for the (c) region of the sample (digenite NC's) at a pump fluence $w_p = 4$ mJ/cm² (pump photon energy is 2.33 eV) are shown in Fig. 2. The spectra are defined as follows: DTS = $(T - T_0)/T_0$, where T_0 and T are the transmission spectra of unexcited and excited samples, respectively. The observed effect is a well pronounced bleaching of the sample concentrated at the spectral position of the ω_3 band. It can be explained by the state-filling-induced saturation of the lowest optical transition in the digenite NC's. The amplitude of the relative absorption changes ($\Delta \alpha / \alpha_0$) reaches ~0.2. The transmission recovery time is of about 3 ns (see inset to Fig. 2) that is at least an order of magnitude

longer than in CdSSe NC's.²² From the recorded DTS the $\chi^{(3)}$ value of $\sim 10^{-7}$ esu can be estimated. This is by 2–3 orders of magnitude larger than in CdSSe-doped glasses.²² Within the two-level model⁵ $\chi^{(3)} \propto N_{nc} f_{cv}^2 \tau_e$, where N_{nc} is the NC concentration in the glass matrix, f_{cv} is the oscillator strength of the interband optical transition, and τ_e is the carrier relaxation time. As shown above, the CdS-to-Cu_xS conversion leads to increased values of both the linear absorption (i.e., oscillator strength) and the carrier lifetime. These are the main factors resulting in the enhancement of the non-linearity.

In conclusion, the Cu_xS NC's with average radius of ~4 nm are grown in the glass matrix originally containing CdS NC's. The prepared nanostructures clearly exhibit the effect of a 3D carrier confinement which is manifested as well resolved peaks in linear absorption. The structure of the absorption spectra shows the presence of the NC's formed by different Cu_xS phases (with *x* ranging from 1.8 to 2). The Cu_xS quantum dots exhibit large optical nonlinearities ($\chi^{(3)} \sim 10^{-7}$ esu), exceeding those observed in CdSSe NC's. The enhanced nonlinearity results from the increased values of the carrier lifetime and the linear absorption.

V. K. acknowledges the support from the Alexander von Humboldt Foundation. P. H. is supported by the Heinrich Hertz Foundation. This work is partly supported by the Russian State Program "Physics of Nanostructures" (Grant No. I-042).

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