Hot photoluminescence in amorphous As_2S_3

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We observe a broad radiative emission spectrum in amorphous As_2S_3 which is positioned around the optical gap. Measuring the polarization memory with respect to the excitation radiation enables us to characterize the radiation process. The radiative recombination can be explained by recombination of hot self-trapped excitons.

At low temperature, amorphous (a-) As_2S_3 exhibits a steady-state photoluminescence (PL) spectrum of wide bandwidth centered at half the optical gap energy.[1] The radiative quantum efficiency is about 20% and the excitation spectrum is peaked slightly below the optical gap energy.[2] This PL has been associated with radiative recombination at defect centers in the energy gap[3] or with small polaron recombination.[4]

Time-resolved PL studies revealed an intricate recombination behavior in a-As_2S_3.[5–9] Furthermore, band-to-band (BB) PL (Ref. 7) was found where the radiative quantum efficiency increases with increasing excitation photon energy.[10] Recently, this BB luminescence has been contested[11] and assigned to organic contamination. The new data were gathered for amorphous hydrogenated silicon (a-Si:H) films utilizing low-repetition-rate, high-pulse-power excitation. Organic contamination is possible for slow-growing vacuum-deposited films but is unlikely for pure quenched bulk glasses like a-As_2S_3. We notice though that the published spectra of the BB luminescence of various materials such as a-As_2S_3 and a-Si:H differ only slightly.[7,12] Thus a reinvestigation of the emission properties about the optical gap is necessary.

We report here a reproducible, intrinsic PL process with lower quantum efficiency and different behavior compared to the so-called BB luminescence. Measurements and sample preparation were performed with the *utmost* care. Highly pure As_2S_3 (59) was sealed into fused quartz tubes, rocked once a minute during 24 hours at 550 °C and then rapidly cooled to room temperature. Commercial samples (Servo Corp.) with flat polished surfaces were also prepared for the measurements. The results were unaltered after cleaning of the *natural* or polished surfaces with organic solvents and/or inorganic etchants. A cavity dumped Ar-ion laser, producing 11-ns pulses with a repetition rate of up to 1 MHz, was utilized to excite the PL which was analyzed by a double-grating monochromator and detected with a fast cooled GaAs photomultiplier. The signal was processed by a computer-based gated photoncounting system. The optical alignment was adjusted for maximal signal of the Raman Stokes line with no delay between the laser pulse and the gating window.

Room- and low-temperature PL spectra are shown in Fig. 1 for excitation photon energy of 2.41 eV. The Raman scattering lines, first-order Stokes at 2.36 eV and second-order Stokes at 2.32 eV, are superimposed on the low-temperature luminescence spectrum. The rise of the PL at lower photon energy corresponds to the high-energy tail of the known emission spectrum[6] which is quenched at room temperature. The contribution of light scattering was tested with high-quality crystalline reference materials such as silicon and quartz. These measurements showed that Rayleigh scattering can be neglected below 2.25 eV. Furthermore, the low minimum at 2.38 eV indicates good discrimination against scattered light. We estimate a radiative quantum efficiency of 5×10^{-5} for an energy close to the optical gap at 300 K.

For the low-temperature measurements the samples were cooled in an oil-free ion-pumped cryostat. In order to handle the samples rapidly, and since the signal-to-noise ratio was sufficient at room temperature, we acquired spectra of free-standing samples. The room-temperature PL spectra for different excitation energies are depicted in Fig. 2. Superimposed

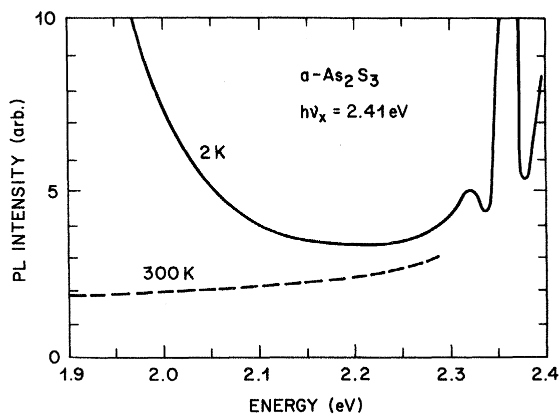

FIG. 1. Photoluminescence band and Raman scattering lines in a-As_2S_3 at 2 and 300 K. $h\nu_x$ is the excitation photon energy. An incident power of 38 mW was utilized.

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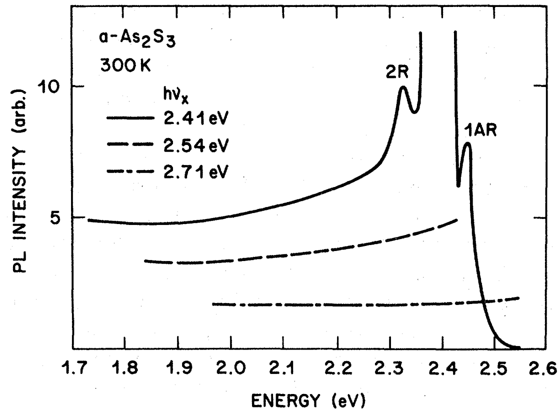

FIG. 2. Room-temperature photoluminescence spectra of a-As_2S_3 for different excitation energies. The spectrum for 2.41-eV irradiation is extended about the excitation energy to show the portion due to light scattering. (The luminescence is plotted in photons/cm^2 eV.)

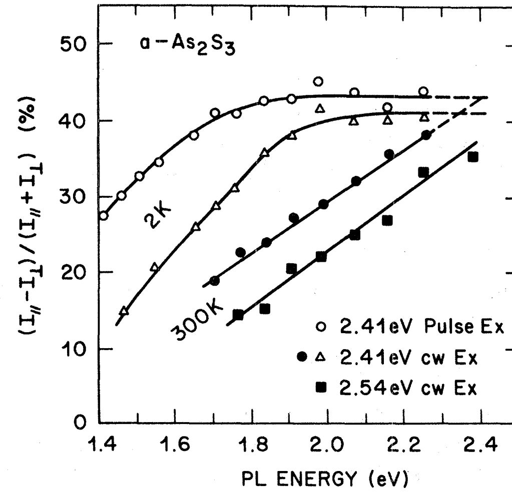

FIG. 3. Polarization memory as a function of photoluminescence energy for various excitation energies.

on the spectrum with an excitation energy of 2.41 eV is also the first-order Raman anti-Stokes line. The luminescence intensity decreases with increasing excitation photon energy, which might be due to the higher probability of carrier separation at higher energy. This behavior is contrary to the quantum efficiency reported for the BB emission.[10]

The optical gap in a-As_2S_3 is $\approx$2.35 eV at room temperature.[3] The PL spectra in Fig. 2 show that radiative emission above the optical gap is observable, but that no appreciable anti-Stokes emission is present for excitation at 2.41 eV. The increase at lower PL energies is due to the remaining midgap PL process. Therefore the high-energy PL process extends from about 2 eV to an energy above the optical gap. A possible explanation for this luminescence behavior is the assumption of hot luminescence of self-trapped excitons. In order to substantiate this claim further, we measured the *polarization* characteristics of the PL. These characteristics can be tested experimentally. We have examined all combinations of the optical arrangement with the limitation of the orientation of our bulky double-grating monochromator.

Polarization memory of the midgap PL at low temperature was reported.[13,14] We measured the PL polarization memory:

$$P=(I_{\parallel}-I_{\perp})/(I_{\parallel}+I_{\perp}) \quad (1)$$

of the high-energy luminescence at 2 and 300 K for two excitation energies. $I_{\parallel}$ is the intensity of the PL component parallel to the polarization direction of the excitation light, and $I_{\perp}$ is perpendicular to it, respectively. The results of the polarization memory measurements are shown in Fig. 3 and reveal several interesting features. The polarization memory is nearly perfect, since the maximal value for an amorphous material of 50% is approached. The shape of the room-temperature PL memory is independent of excitation energy. The PL memory decreases with decreasing PL energy, which is expected if the excitation is decaying stepwise. At low temperature the PL memory is constant above 2.0 eV, which indicates two different decay mechanisms for the range of the hot PL. Furthermore, the PL memory observed within 10 ns (pulsed excitation) is higher than for continuous-wave (cw) excitation in agreement with expectation from time-resolved measurements.[6,15] It is also remarkable that the polarization memory for low and room temperature approaches the same value at high energy.

The PL polarization memory supports the interpretation that the underlying mechanism is hot PL from self-trapped excitons (STE). The dissipation of the excess energy is divided in two possible channels: The first channel (a) is representative of a process where the self-trapped exciton thermalizes at the same site. The hot PL produced along with phonon emission retains its memory for polarization with respect to the excitation radiation. A second process (b) is assumed in which the self-trapped exciton hops to another site during phonon emission. In this case the PL process loses its polarization memory.

We calculate now the PL polarization memory under the assumption of energy dissipation into two processes. The polarization memory for processes a and b is given by

$$P=(I^a_{\parallel}-I^a_{\perp})/(I^a_{\parallel}+I^a_{\perp}+I^b) \ . \quad (2)$$

I^a and I^b are the luminescence intensities of process a and b. The probability of the STE remaining at the

same site after emission of n phonons is

$$(1-q)^n \ , \tag{3}$$

where q is the ratio of the hopping rate to the relaxation rate of the STE. If P^a is the polarization memory for process a, the total polarization memory is then

$$P = P^a(1-q)^n \tag{4}$$

At this point we assume $q \ll 1$ and express the phonon number as

$$n \approx (E_x - E_L)/\hbar\Omega \ . \tag{5}$$

E_x and E_L are the excitation and luminescence energies, respectively, and $\hbar\Omega$ is the phonon energy. With these simplifications the polarization memory is

$$P \approx P^a\left[1 - \frac{(E_x - E_L)}{\hbar\Omega}q\right] \ . \tag{6}$$

Fitting Eq. (6) to the experimental data of Fig. 3 at room temperature gives $q = 0.05$ and $P^a = 43\%$. Assuming a relaxation rate of the STE of $\approx 10^{12}\ s^{-1}$, we estimate a hopping rate of $< 5 \times 10^{10}\ s^{-1}$. This hopping rate is in reasonable agreement with estimated values for polaronic motion.[16]

The hopping rate for the STE will decrease with decreasing temperature. Therefore, according to Eq. (6), the polarization memory of the hot luminescence will approach a constant value P^a at low temperature. Finally, the quantum efficiency of the hot luminescence is given by the probability of STE generation, the loss of STE due to carrier separation, and by nonradiative recombination. With this in mind, one expects a decrease of the PL with increasing excitation energy as the carrier breakup is aided by the extra kinetic energy.

In summary, we describe a broad bandwidth photoluminescence at the optical gap in a-As_2S_3. This emission exhibits high polarization memory for the excitation radiation and is consistent with the assumption of hot luminescence of self-trapped excitons.

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