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Time-Resolved Photoluminescence Spectroscopy in Amorphous As$_2$S$_3$

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Measurements of time-resolved photoluminescence spectra at 2 K from amorphous As$_2$S$_3$ on a 10-nsec time scale demonstrate that two independent luminescence processes exist simultaneously. The higher-energy luminescence process at 1.75 eV has a very short lifetime and is rapidly quenched at higher temperatures. The other process appears at lower energy (1.45 eV) and shifts to considerably lower energy with increasing time delay. A model to explain this result is proposed.

Localized states in the gap of amorphous solids are believed to be responsible for many unique properties of these materials. Several models, incorporating Anderson's idea of the negative correlation energy,[1] have been proposed to explain the microscopic origin of these defect states.[2-5] Photoluminescence is a powerful tool for studying these localized states.[6-8] We show that investigations of the dynamics of photoluminescence processes provide new insight into the nature of localized states in amorphous solids.

We report the first measurements of the time evolution of the photoluminescence spectra from an amorphous solid (a-As$_2$S$_3$) with 10-nsec time resolution. A single, fast luminescence process, occurring at $\frac{2}{3}$ band-gap energy and decaying within the time resolution of 10 nsec, was recently reported by Murayama et $al.$[8] In contrast to this, our measurements reveal that (1) two independent luminescence processes occur simultaneously in a-As$_2$S$_3$ at short times, (2) these processes are independent of samples, (3) the high-energy process (HEP) decays rapidly in time without any spectral shift and is very strongly temperature dependent, and (4) the spectrum of the low-energy process (LEP) shifts drastically to lower energy with increasing time delay (τ). For $\tau > 200$ nsec, the spectrum becomes similar to the half–band-gap luminescence observed in cw or long-pulse excitation, thus establishing a connection between the short- and long-time processes. We present a model to explain these observations, which cannot be adequately understood by existing models of defect states. Furthermore, the observed properties of the HEP are different from the properties of excitons recently discussed by Street.[7] In this case, our results indicate that additional states in the forbid-

den gap would be required to explain its presence in a defect model.

Three different sources of high-purity a-As_2S_3 have been used in the present experiment and no sample dependence has been found. One sample was polished in the form of an overhemisphere, improving the collection of the luminescence by more than an order of magnitude. The sample was mounted in a Varitemp cryostat and excited by an unfocused (spot diameter ≈ 1 mm) beam from a cavity-dumped argon laser operated at 2.54 eV (488.0 nm, where the absorption coefficient is $\alpha \approx 2000$ cm^{-1}). The full width of the exciting laser pulse at half maximum was 11 nsec. In order to minimize fatiguing (decrease in luminescence intensity with prolonged excitation), the incident peak power was $\leqslant 1.3$ W with an average power of $\leqslant 0.5$ mW. The luminescence was dispersed by a $\frac{3}{4}$-m grating spectrometer (spectral resolution of 5 nm) and detected by a cooled fast S-1 photomultiplier followed by a gated (10-nsec gate width) photon counter. Time-resolved spectra were obtained by scanning the spectrometer at a fixed gate delay τ and time evolution at fixed wavelength was obtained by scanning the gate delay.

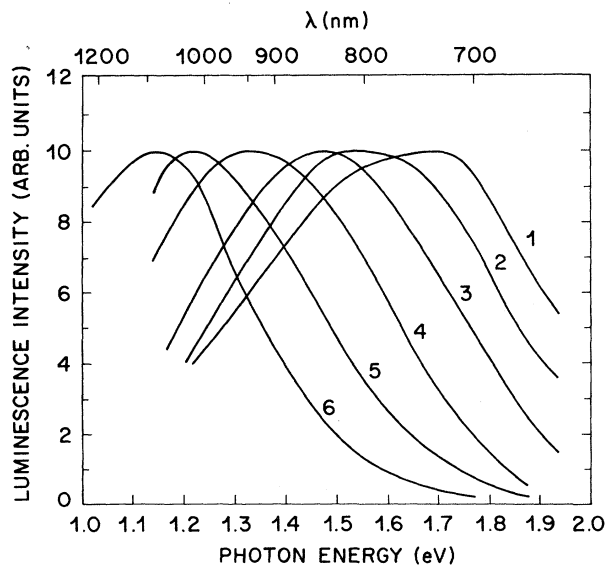In Fig. 1 we show the photoluminescence spectra, normalized and corrected for the system response, at 2 K for various delays τ. For $\tau = 0$, we observe an unresolved double peak. With increasing τ, the spectrum shifts continuously to lower energy and becomes narrower and more symmetric. For $\tau > 200$ nsec only slight changes in the spectral response have been observed.[7] In Fig. 2 we show the spectra at $\tau = 0$ for three different temperatures. The high-energy process (1.75 eV) disappears very rapidly with increasing temperature. The spectrum at 100 K is narrower, more symmetrical and has a peak at 1.45 eV, which is still quite far from the peak in the cw spectrum. In Fig. 3, the detection system response at the laser wavelength is compared to the time evolution of the luminescence for the LEP and HEP. At 700 nm, the luminescence decays in a time slightly longer than the system response time. The luminescence has decayed to less than one percent of its peak value at approximately 100 nsec. The behavior at 940 nm is quite different. The luminescence initially decays rapidly but then the rate of decay slows down considerably.

The data presented above show that two luminescence processes (LEP and HEP) occur simultaneously in a-As_2S_3 at short times and low temperatures. Although the two processes do not result in two well-resolved spectral peaks, their existence can be established by noting the following: (1) The shape of curve 1 in Fig. 1 is very asymmetric (the cw luminescence from amorph-
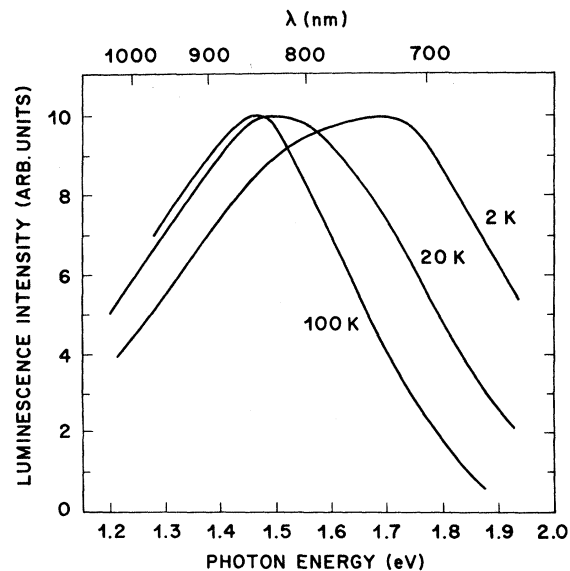

FIG. 1. Normalized, time-resolved luminescence spectra of a-As_2S_3 at 2 K for various delays and an excitation wavelength of 488.0 nm. The delays are (1) 0, (2) 10, (3) 20, (4) 70, and (5) 160 nsec. 0 delay corresponds to the gate at the laser peak. Curve 6 is the cw spectrum from Ref. 6.

FIG. 2. Normalized luminescence spectra of a-As_2S_3 at 0 delay for three temperatures.
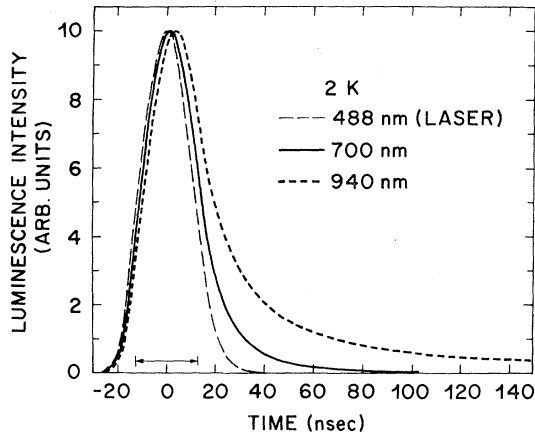
FIG. 3. Normalized time-evolution curves at three wavelengths. The curve at 488.0 nm is the system response. The arrow indicates the total duration of the exciting laser pulse as measured by a fast photodetector and oscilloscope.

ous chalcogenides exhibits a broad near-Gaussian shape due to phonon broadening.[7] (2) Curves 2 and 3 in Fig. 1 show that the HEP disappears very rapidly with increasing delay. This is to be contrasted with the slow spectral shift of LEP with τ. (3) The intensity of the HEP diminishes extremely rapid with increasing temperature (Fig. 2), in contrast with the behavior of the LEP.

This is the first time that the existence of two simultaneously occurring, independent luminescence processes has been established in an amorphous chalcogenide. Murayama et al.[8] observed a single, sample-dependent luminescence process at approximately the same spectral position as the HEP, which decayed within their time resolution of 10 nsec and which was attributed to radiative recombination of excitons. The relation of this process to the HEP is unclear at present because the excitation intensity used in our experiment is many orders of magnitude smaller. The HEP is unlikely to be due to excitons for the following reasons: According to Street,[7] the extremely strong coupling between excitons and phonons[9] in amorphous chalcogenides will lead to a very short lifetime (10^{-11} sec) and low quantum efficiency (10^{-3}) for excitons. Time evolution data in Fig. 3 show that HEP has a time constant of the order of 10 nesc. Furthermore, the ratio of quantum efficiencies at 700 and 940 nm (as measured from the complete time-decay curves) is approximately 0.1 leading to a quantum efficiency of 2%[10] for the HEP. Also the rapid decrease in the intensity of the HEP with temperature argues against the exciton picture. It is thus clear that HEP is either not due to an exciton with properties different from those described by Street.

If one assumes that the HEP is not due to an exciton, defect states in the gap could be considered to account for it. According to the Street and Mott (SM) model,[2] the cw luminescence arises from an electron in the conduction band recombining with a hole trapped at a D^- center arising from dangling bonds. The corresponding process of a hole recombining with a trapped electron at a D^+ is expected to occur at a lower energy[7] and hence cannot be responsible for the HEP. One would then be forced to admit the existence of defect states other than D^+, D^-, and D^0 introduced in the SM model.

Kastner, Adler, and Fritzsche and Kastner[11] have introduced other defect states such as valence-alternation pairs (VAP), intimate VAP (IVAP), and states arising from lone-pair-configuration distortions (LCD). Since VAP's and IVAP's cannot both coexist in a given material, we consider only IVAP's and LCD's. Within this model the cw luminescence is explained in IVAP's. However, the HEP cannot be explained by LCD's which are thought to be nonradiative centers.[11] It appears that modifications of the the model will be required to account for the HEP.

We now turn our attention to the LEP. The spectrum of the LEP gradually shifts to lower energies with increasing time delay and becomes similar to the cw luminescence spectrum at very long delays.[12] Since changes occur on tens of nanoseconds, and since lattice relaxation is expected to be much faster, we rule out the possibility that relaxation in the configuration coordinate is responsible for the observed behavior. One possible explanation of the LEP may be obtained by an extension of the SM model. We propose that the observed luminescence arises when an electron in any one of the localized band-tail states in the conduction band recombines with a hole trapped at a D^- center. At short times, the recombination process is dominated by the electrons in the shallower states near the mobility edge. Since the wave function of electrons in these shallow states have a larger spatial extent than those in deeper states, it is expected that the lifetime of electrons in these shallow states is rather short. Therefore, the population of electrons from these shallow states will be depleted more quickly than from the deeper states;

also, some of these electrons might hop to more tightly bound states. This will lead to a shift in the spectrum to lower energy. At long times, electrons will occupy only the deep band-tail states and will give rise to a spectrum at low energy which will not shift with time any further.[13] According to this model, the shift in the spectral peak should be approximately equal to the width of the band-tail states. The width of conduction band-tail states, estimated to be approximately 0.2 eV,[14] is in reasonable agreement with the observed shift of slightly more than 0.2 eV between curves 4 and 6 in Fig. 1. Another consequence of this model would be that at short times the spectral width would be the sum of the phonon broadening (as observed in the cw spectrum) and the width of the band-tail states. Figure 1 shows that there is a reduction in the observed width of the luminescence spectra with increasing time delay, in agreement with the proposed model.

Finally, we would like to draw attention to the fact that at 940 nm there is a fast initial decay of the luminescence intensity and a very slow final decay of intensity. Thus the lifetimes of centers involved in luminescence process vary by several orders of magnitude, depending on their spatial separation. At higher energies (e.g., 800 nm), the spread in decay-time constant is not observed to be so large; this may be attributed to larger spatial extent of the electron wave function in the shallower conduction-band–tail states.

In conclusion, we have demonstrated the existence of two independent luminescence processes in a-As_2S_3 by applying the techniques of nanosecond time-resolved spectroscopy to an amorphous solid. Properties of the high-energy process are different from those ascribed to an exciton in such materials. We therefore conclude that either the exciton has very different properties, or defect states other than those required to explain the cw luminescence in a defect model would have to be present. We have also shown that the spectrum of the low-energy process gradually shifts in time to lower energies. A model to explain

this shift is proposed.

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[12]D. Emin [see Ref. 11, p. 261] has proposed that most properties of amorphous chalcogenides can be explained by the formation of small polarons. In this case, the observed luminescence would be due to radiative recombination of small polarons.

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