Above-band-gap emission in amorphous semiconductors:
Localized states versus surface contamination

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The nature of the above-band-gap emission which has been reported by Shah and co-workers in a number of amorphous semiconductors is investigated. The remarkable features of this emission have been attributed to unique properties of the electronic states in these materials. Similar features have been observed in other materials, however, where they were ascribed to contamination effects. Using the Raman phonon spectrum for calibration, this study finds the intensity of the emission from amorphous silicon to be sensitive to surface cleaning procedures. This suggests that the above-band-gap emission may be due to surface contamination, and unrelated to bulk states in the material. A simple model describing the optical properties of a mixture of organic contaminants is proposed which is capable of reproducing the essential features.

Above-band-gap emission has been reported recently in a number of amorphous semiconductors including chalcogenide glasses[1] and amorphous silicon.[2] This broad emission exhibits many remarkable characteristics, the most notable being that it can extend 1 eV or more above the optical-absorption gap of the material. Even the peak can occur above the gap. The decay following pulsed excitation is too fast to be resolved with 10-ns time resolution, and the intensity varies essentially linearly with laser power. The peak shifts to higher energy as the exciting frequency, ν_{ex}, is increased, but the shift of the peak is smaller than the change in ν_{ex}. The width and intensity also increase with ν_{ex}. Thus the emission behaves neither like a scattering process, nor a simple fluorescence. The spectrum is essentially independent of temperature, except for an anti-Stokes tail that grows with temperature. The intensity also shows only a weak temperature dependence. Since such an emission process is not generally observed in crystalline materials, it has been thought to indicate unique properties of the electronic states in amorphous solids. Unfortunately, the results reported here on a-Si indicate the plausibility of an alternate explanation: the emission may simply be fluorescence from organic surface contaminants present in the laboratory environment.

The unusual characteristics of the emission have prompted a number of attempts at modeling the phenomenon in terms of electronic states peculiar to amorphous semiconductors. In the widely considered model concerning the effects of disorder first proposed by Mott,[3] photoexcitation above the bandgap is expected to populate extended states that thermalize rapidly to the band edge, leaving at most a thermally activated exponential tail in the emission from above the band edge. Within this framework, the observed emission, whose peak can be well above the band gap, has been attributed to a nonthermalized carrier distribution, indicating that the electronic states remain somewhat localized far above the band edge.[1]

Photoconductivity (PC) measurements in a-Si, however, appear to be more consistent with fast carrier thermalization. the nonexponential decay and the thermal activation of the measured mobility can be successfully modeled assuming thermal emisssion from shallow-band-tail states into a highly mobile conduction band.[4] This implies that thermalization to the band edge in a-Si occurs more rapidly than the few ps time resolution of these PC measurements. In those a-Si samples with a high defect concentration, trapping into even deeper levels occurs within a 10-ps time scale, as is also thought to be the case for chalcogenide glasses.[5] This leaves little possibility of any localized states remaining populated far above the band edge. Finally, the high initial mobility measured for a-Si samples of varying defect concentration,[4] and inferred for the chalcogenides,[5] also mitigates against any localization in the conduction-band states.

An alternate description of the source of the above-band-gap emission has been suggested[6] within the Anderson "negative-U" model.[7] In this picture, the electronic energy levels of doubly occupied states have no gap at the Fermi energy, E_F. Nevertheless, states near E_F have a large negative effective electron correlation energy, U, associated with them. Consequently, excitation of a single electron from these highly localized states near E_F may actually require more energy than band to band transitions. Photoexcitation above the band gap may then excite both extended states, resulting in a photoconductivity signal,

while at the same time exciting some of these local-
ized states which may subsequently decay producing
the above-band-gap emission. Other aspects of the
observed emission do not fit this picture so well. For
example, the lack of temperature dependence of the
intensity is disturbing, as is the close quantitative
resemblance in spectra from materials assumed to
have rather different band gaps and Stokes shifts.

The widespread speculation about the electronic
states responsible for this emission has been due, at
least in part, to the apparent novelty of its charac-
teristics. In fact, however, there are at least a few re-
ports of similar behavior, and apparently numerous
unreported observations in liquids, glasses, and crys-
tals in light scattering experiments,[8] which are partic-
ularly sensitive to weak emission signals. Strong sig-
nals with similar features have been reported in
Vycor[9] (porous quartz) and other high-surface-area
materials used in catalysis,[10] when pumped with Ar
laser lines. The spectra are similar to those observed
in a-Si and the chalcogenides. With increasing laser
frequency they broaden and intensify, and they also
shift, again less than one to one. In the case of
quartz, however, the intensity can be varied by or-
ders of magnitude depending on surface preparation.
As a result, organic surface contamination has been
postulated to be responsible. Of course, in this case
there is no question of any conduction band involve-
ment, as it lies another 5 eV higher in energy.
Although the reported signal from a-Si or the chal-
cogenides is orders of magnitude weaker, the effec-
tive surface area is comparatively smaller. Conse-
quently, in order to investigate the possibility that the
amorphous semiconductor emission is also due to
surface contamination, I have studied the intensity of
the emission from a-Si as a function of surface
preparation.

The a-Si films used in this investigation include 6
samples grown by rf glow discharge on crystalline Si
and quartz substrates, and 2 UHV evaporated films.
The samples were excited with a 10-Hz Nd:YAG (yt-
trium aluminum garnet) pumped dye laser with a
10-ns pulse length and ~2 mW average power, light-
ly focused to a 1×2 mm^2 spot. The beam was
passed through a monochromator to remove broad-
band dye fluorescence. The radiation from the sam-
ples was dispersed with a double monochromator and
detected with an S-20 photomultiplier with a 20-ns
response time, followed by a gated boxcar integrator
whose 15-ns gate was set coincident with the laser
pulse. The strength of the radiation was calibrated by
comparison with the Raman phonon peat at ~480
cm^{-1},[11] using 70-cm^{-1} resolution. As it became ap-
parent that similar broadband emissions are ubiqui-
tous in the laboratory, and many sources are much
stronger than the sample itself, extreme care was tak-
en to shield the collection optics from any other sur-
faces illuminated by scattered laser light.

All off-the-shelf samples, both UHV evaporated
and glow discharge, exhibited a broad emission simi-
lar to previous reports, as shown in Fig. 1. The peak
intensity was comparable to or greater than the Ra-
man phonon mode (at 70-cm^{-1} resolution), also in
agreement with earlier work.[2] Fresh samples—those
less than one day old—often had somewhat weaker
signals. The broad emission behaved as described in
the literature: the position, width, and intensity were
dependent on the laser frequency and the decay of
the signal following the laser pulse was faster than
the ~30-ns system response. There was no indica-
tion of any nonlinearity with laser power.

As found for porous quartz, however, the emission
intensity could be greatly reduced by appropriate sur-
face preparation, in this case by cleaning. As shown
in Fig. 2, careful cleaning with methanol in which the
solvent is pulled off the sample with a lens tissue, re-
duced the broadband signal considerably in a-Si:H.
Vapor degreasing with trichloroethylene reduced the
signal level below background noise levels: factors of
at least 15 and 25 below the Raman phonon peak at
pump frequencies of 20 500 cm^{-1} (~4880 Å) and
19 450 cm^{-1} (~5145 Å), respectively. The reference
Raman phonon spectrum shown in Fig. 2 was un-
changed by cleaning, or by the laser excitation during
the measurement of the broadband spectrum. If the
sample was subsequently allowed to sit for a few days
in the laboratory environment, or if any methanol
was allowed to dry on the sample during cleaning, the
signal returned. Care also had to be taken to aviod
any dust on the sample which can result in a tenfold
increase in the signal strength, as indicated in Fig. 2.
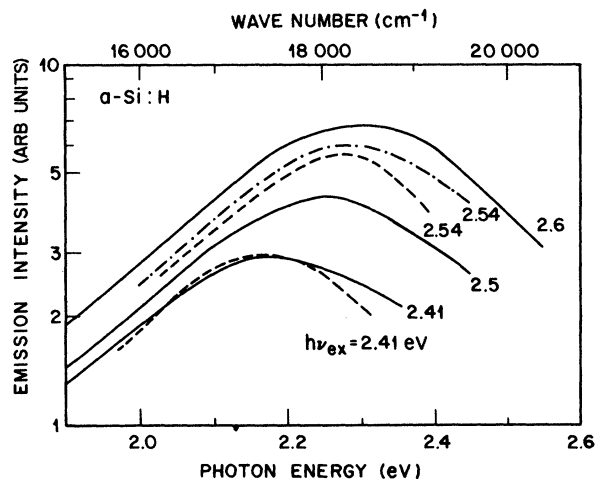Samples cleaned repetitively with lens tissues eventu-

FIG. 1. Above-band-gap emission spectra in a-Si:H. Solid
curves from Ref. 2, dashed curves this study. Dash-dot
curve is a bulk sample of pump oil. The relative strengths
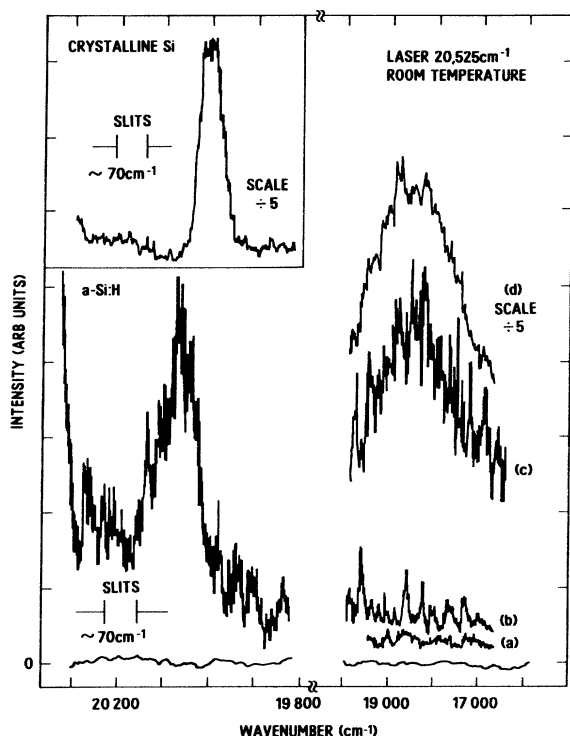of the dashed and dash-dot curves are arbitrary.

FIG. 2. Strength of above-band-gap emission in a-Si:H as a function of cleaning procedures described in text. The Raman phonon spectrum is shown to scale at left. (a) After vapor degreasing, (b) after methanol cleaning, (c) off the shelf, and (d) beam hitting dust speck. At upper left a crystalline Si Raman spectrum is shown for comparison.

ally showed damage—the apparent shine was reduced—and further cleaning no longer reduced the signal.

This sensitivity to cleaning procedures strongly suggests that the anomalous emission in a-Si is due to surface contamination, and unrelated to bulk states in the amorphous film. Any remnent broadband emission originating from the bulk of the film must apparently be exceedingly weak— $< \frac{1}{25}$th of the Raman phonon intensity excited by 19 450 cm^{-1}, and would itself be suspect—bulk contamination of the film is also possible during sample growth. The similarity of the emission reported in chalcogenide glasses suggests that it too may be due to surface contaminants. In chalcogenides, the lack of signal fatigue has also been interpreted as indicative of a surface effect, as the fatigue is thought to be a result of competing absorption processes in the bulk.[12] Chalcogenide glasses have not been included in this study due to their extreme sensitivity to laser damage, especially at the high peak powers used here.

Surface contaminants could easily reproduce the essential features of the anomalous emission. The composite spectrum of a mixture of many fluorescing organics would be a broad featureless band whose

peak would shift with ν_{ex} due to selective excitation of different subsets of the mixture. The observed intensity and width increase when pumping in the blue is consistent with the less extensive variety of organic species which absorb in the red. Some examples of organic mixtures that I have observed to behave in precisely this fashion are forepump oil, finger oil, and wood or cloth fibers—all common contaminants in the laboratory environment. The spectrum of a pump oil sample is shown for comparison in Fig. 1. The fluorescence from bulk samples is quite strong—only miniscule amounts of the sample surfaces could account for the observed weak signal levels.

Although it seems clear that the source of the above-band-gap emission is some form of surface contamination, this particular model leaves a few unanswered questions. First, the decay time is rather fast for many fluorescing organics such as naphthalene derivatives whose lifetimes are more commonly in the tens of ns. Secondly, although the generally weak temperature dependence is consistent with high quantum efficiency fluorescing species, the reported rise in intensity of the emission[2] from a-Si:H between 2 and 50 K is difficult to reconcile with this model. Since the subband luminescence in a-Si:H follows this same pattern,[13] some involvement of the underlying substrate would seem to be implied. There are also slight, but reproducible differences in the spectra from different materials, although this may merely indicate a sample dependence of the affinity to adsorb certain species.

In summary, I have examined various models of the above-band-gap emission in amorphous semiconductors. The unusual characteristics of this emission have led to much speculation on the nature of the electronic states in amorphous semiconductors, but the data presented here indicate the plausibility of an entirely different explanation. The signal intensity in a-Si was shown to be extremely sensitive to the cleanliness of the surface. This is a strong indication that the emission originates from surface contaminants, rather than bulk states in the amorphous film, and a simple model of a mixture of fluorescing organic species was shown to reproduce the essential features. Clearly extreme caution must be exercised when identifying any broad, fast, temperature insensitive emission that shifts with laser frequency, as an intrinsic characteristic of a particular material.

[1]J. Shah and M. A. Bosch, Phys. Rev. Lett. **42**, 1420 (1979); Solid State Commun. **31**, 769 (1979); J. Shah and P. M. Bridenbaugh, *ibid.* **34**, 101 (1980).

[2]J. Shah, F. B. Alexander, Jr., and B. G. Bagley, Solid State Commun. **36**, 195 (1980); and J. Shah (private communication).

[3]N. F. Mott, Adv. Phys. **16**, 49 (1967).

[4]A. M. Johnson, D. H. Auston, P. R. Smith, J. C. Bean, J. P. Harbison, and D. Kaplan, in *Chemical Physics: Picosecond Phenomena II,* edited by R. M. Hochstrasser, W. Kaiser, and C. V. Shank (Springer Verlag, New York, 1980), Vol. 14, p. 285; A. M. Johnson and D. H. Auston (private communication).

[5]R. L. Fork, C. V. Shank, A. M. Glass, A. Migno, M. A. Bosch, and J. Shah, Phys. Rev. Lett. **43**, 394 (1979); D. E. Ackley, J. Tauc, and W. Paul, J. Non-Cryst. Solids **35/36**, 957 (1980); Joseph Orenstein and Marc Kastner,

Phys. Rev. Lett. **43**, 161 (1979).

[6]R. Fisch and D. C. Licciardello, Phys. Rev. Lett. **41**, 889 (1978); and D. C. Licciardello (private communication).

[7]P. W. Anderson, Phys. Rev. Lett. **34**, 953 (1975).

[8]C. A. Murray, T. H. Wood, K. B. Lyons, J. E. Griffith, and W. Proffitt (private communications).

[9]Cherry Ann Murray and Thomas J. Greytak, Phys. Rev. B **20**, 3368 (1979).

[10]T. A. Egerton and A. H. Hardin, Catal. Rev. Sci. Eng. **11**, 71 (1975).

[11]J. E. Smith, Jr., M. H. Brodsky, B. L. Crowder, and M. I. Nathan, Phys. Rev. Lett. **26**, 642 (1971).

[12]M. Kastner and S. J. Hudgens, Philos. Mag. B **37**, 665 (1978); and M. Kastner (private communication).

[13]J. Shah, B. G. Bagley, and F. B. Alexander, Jr., Solid State Commun. **36**, 199 (1980); C. Tsang and R. A. Street, Phys. Rev. B **19**, 3027 (1979).