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Stimulated photoluminescence in indium selenide

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The stimulated emission from the layered indirect-gap semiconductor InSe under high values of dye laser excitation intensity has been investigated in the temperature range 20—300 K. The emission intensity dependences on the laser intensity, on the excited length of the sample, and on the temperature are reported; optical gain spectra and quantum efficiency measurements have been also performed. We have evidence of four light amplification processes, in the near-infrared region, associated either with cooperative excitonic interaction or with electron-hole plasma recombination.

INTRODUCTION

Indium selenide is an indirect-gap layered semiconductor (space group D_{6h}^4) with the top of the valence band located at the center Γ of the Brillouin zone (Γ_1^+ symmetry) and the bottom of the conduction band situated at the K point (K_2 symmetry). Moreover, a relative minimum of the conduction band (Γ_1^-) at Γ point is found to be at 54 meV above the minimum of the K point. The fundamental direct and indirect gaps at 90 K are, respectively, $E_g^d = 1.339$ eV (Ref. 1) and $E_g^i = 1.285$ eV.[2,3] The direct free exciton (FE) associated with the minimum Γ_1^- shows a binding energy of 14.5 meV. As a consequence of the crystal structure this FE becomes, according to Phillips,[4] a resonant state with the continuum of free-electrons states of the indirect conduction band bottom, since impurities and phonon scattering can strongly couple the two kinds of states.

The large oscillator strength[1] of the direct free-exciton transition can give FE recombination at energies slightly higher than the E_g^i. These processes become more probable if the temperature is relatively high enough to allow electrons in the K point to jump on the FE levels, and are also favored by high excitation density (HED).

In this paper we report for the first time a systematical study of the stimulated emission from InSe at HED by means of high peak power laser excitation. Four different stimulated emission lines have been observed; three of them (P, P', and X) are localized in the energy range between E_g^d and E_g^i, whereas the fourth (I) is below E_g^i.

On the basis of our experimental data, the nature of the optical amplification mechanisms responsible for P, P', and I lines is associated with cooperative excitonic processes, whereas the X line is ascribed to a no-phonon, electron-hole plasma recombination.

EXPERIMENTAL

The InSe crystals were grown by means of the Bridgmann Stockbarger method starting from a nonstoichiometric melt, containing an In excess of about 5%.[5] They were mounted in variable-temperature cryostat operating by means of a closed-cycle helium refrigerator. The temperature of the sample could be varied and taken constant in the range 20—300 K. The samples were excited by a flow-type nitrogen pumped dye laser, single mode operating at 583 nm with Rhodamin 6 G. The peak power was 0.5 MW with a repetition rate of 100 pulses/sec and a pulse duration of 1 nsec. The optoelectric detection apparatus for both spontaneous and stimulated emission has been described elsewhere.[6] The optical gain spectra were obtained by means of the unidimensional amplifier technique.[7]

RESULTS

The emission spectra of InSe in the energy range between E_g^d and E_g^i will be presented first. The

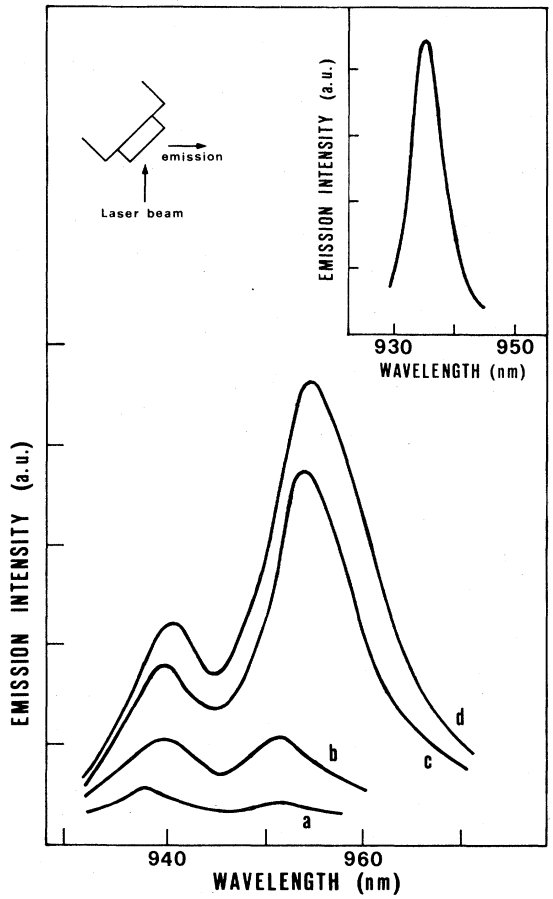

FIG. 1. Spontaneous emission spectra of InSe at 90 K under dye laser excitation: curve *a* 40 kW/cm^2, curve *b* 100 kW/cm^2, curve *c* 250 kW/cm^2, and curve *d* 400 kW/cm^2. The inset shows the emission spectrum under 10-mW He-Ne laser excitation.

spectra at energies below E_g^i will follow. Figure 1 shows a set of spectra obtained from InSe at 90 K in "spontaneous" geometry for increasing levels of dye laser ($\lambda=583$ nm) excitation intensity up to 0.4 MW/cm^2. In the inset, the low excitation spectrum obtained under 10 mW He-Ne laser pumping is shown for comparison. This spectrum consists in only one emission band that can be ascribed to direct free-exciton (FE) recombination, according to the absorption measurements at 90 K.[1,8] In fact we find that the FE emission peak shifts linearly with temperature up to 300 K at a rate $dE/dT=-3.5\times10^{-4}$ eV/K; the temperature dependence of the half-width fits well with the equation

$$H^2(T)=H^2(0)\coth\frac{h\nu_{\rm ph}}{2kT},$$

where $h\nu_{ph}\simeq17$ meV is the average energy of the phonons involved in line broadening.

Figure 1 shows that at HED a new band (*P*) appears at 19 meV below the FE line. With increasing the excitation intensity both FE and *P* lines shift towards lower energies. The shift rate of *P* line is higher since it is due not only to the local heating of the sample but also to the specific recombination mechanism; therefore it is also observed when only the excited length of the sample is increased[9] and excitation intensity is taken constant. The *P*-line peak intensity grows superlinearly with I_0 and is quadratic versus the FE peak; the thermal shift rate of the *P* line is $dE/dT=-3.9\times10^{-4}$ eV/K.

In Fig. 2 the stimulated emission spectra at 90 K obtained at two different levels of HED are reported; the spontaneous spectrum is shown for comparison. At $I_0=0.4$ MW/cm^2 the stimulated emission of the *P* line ($\lambda=958$ nm) only is observed; its half-width is 4 meV, i.e., one half of kT. The experimental thermal shift up to 250 K is $dE/dT=-4.3\times10^{-4}$ eV/K; the external quantum efficiency at 90 K is about 2%. At ten times higher pumping, the stimulated emission consists mainly in the *X* line, centered at 963 nm at 90 K, i.e., 30 meV below the FE; the half-width, larger than for the *P* line, increases with the HED level. For intermediate pumping levels both *P* and *X* lines are observed. At any fixed temperature, if I_0 is increased the *X*-line intensity grows more than the *P*-line intensity. If I_0 is taken constant, a temperature increase induces a decrease for both *P* and *X* lines stimulated emission. This decrease is larger for the *X* line than for the *P* line and shows that the radiative mechanism associated to *X* line is more favored at low temperatures, as confirmed by the spectra at 20 K reported below (Fig. 4) in which the *X* line is dominant.

In Fig. 3 two unsaturated optical gain spectra for the energy range between E_g^d and E_g^i are reported. They were obtained for two different levels of HED, at 90 K, by means of the unidimensional amplifier technique. It is evident that in InSe two population inversion mechanisms are present, related to *P* and *X* lines, respectively, with different intensity threshold. The optical gain associated with the *X* line is observed only for a photoinjected pairs density above the threshold $n_c\simeq10^{17}$ pairs/cm^3 and grows with I_0, while the *P* line's gain decreases. The emitted intensity as a function of the excited length of the sample saturates at lower values for the *P* line than for the *X* line one.

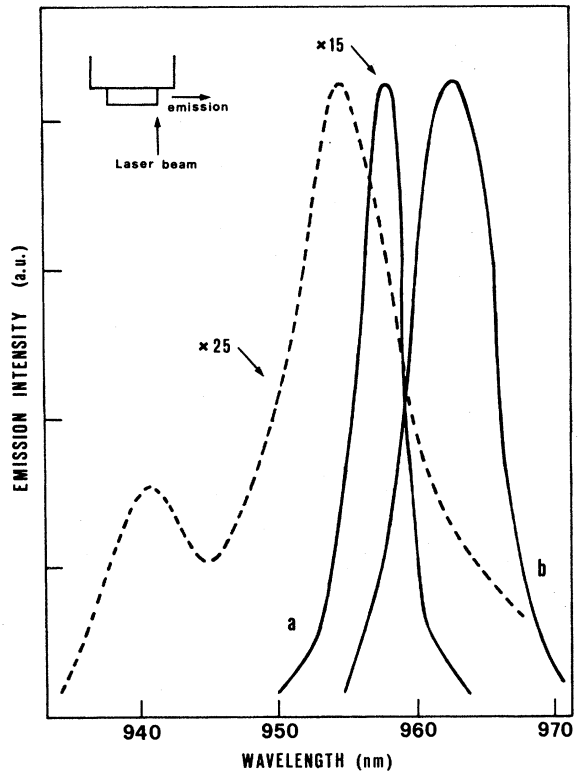

FIG. 2. Stimulated emission spectra of InSe at 90 K under sample edge laser excitation: curve *a* 0.4 MW/cm^2 and curve *b* 4 MW/cm^2. The dashed line shows the spontaneous emission spectrum at 90 K under 200 kW/cm^2 dye laser excitation.

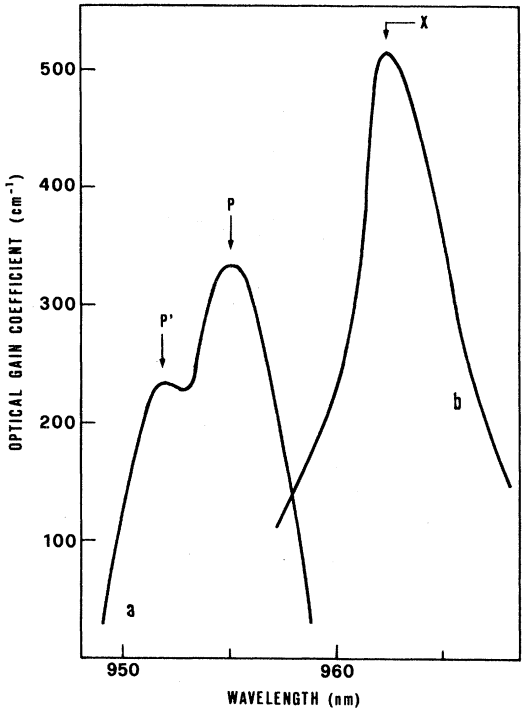

FIG. 3. Optical gain spectra of InSe at 90 K under dye laser excitation: curve *a* 0.4 MW/cm^2 and curve *b* 2.5 MW/cm^2.

For HED levels below the threshold n_c another optical gain band P' ($\lambda=951$ nm) is observed together with the one associated with the P line. The P' gain band is located 14 meV below the FE; in the emission spectra the P' line, whose gain quickly saturates, is easily overcome by the P line.

In Fig. 4 a set of HED stimulated emission spectra at 20 K is reported. It is worth noting that even at relatively low pumping levels the spectra mainly consist in X line, that shifts to lower energies with the excitation intensity and has an asymmetric line shape, with a low-energy tail at the highest pumping. The total external quantum efficiency is now of about 5%.

Stimulated emission in the optical region below E_g^i is observed if, at the highest pumping levels, the distance between the excited region and the sample edge is increased from zero to some tenth of microns. In this case in all the InSe samples we investigated, a new I band appears, as reported in Fig. 5, at 981 nm ($T=90$ K), i.e., about 1.263 eV, then well below $E_g^i \simeq 1.285$ eV. We find that the I-line dependences on temperature and excitation intensity are similar to those of P line. In the pumping arrangement of Fig. 5 the optical gain spectrum has been measured at $I_0=4$ MW/cm^2; two maxima, associated with the X and I lines, respectively, are observed. It is worth noting that the gain coefficient of the I line is about the same as that of the X line in this configuration, as shown in Fig. 6.

DISCUSSION

In the energy range between E_g^d and E_g^i three stimulated emission channels, associated with the P, P', and X lines, respectively, work at different HED levels. For the P line, the observed superlinear dependence on excitation intensity I_0 rules out impurity emission, bound exciton recombination or FE-phonon replicas as its own radiative mechanisms. The intensity dependence on FE, the thermal shift, and the shift with either excitation intensity or excited length suggest that cooperative processes can be the origin of the P line. Two different mechanisms can be considered for the P line stimulated emission: exciton-exciton scattering and exciton-carrier scattering. The intensity depen-

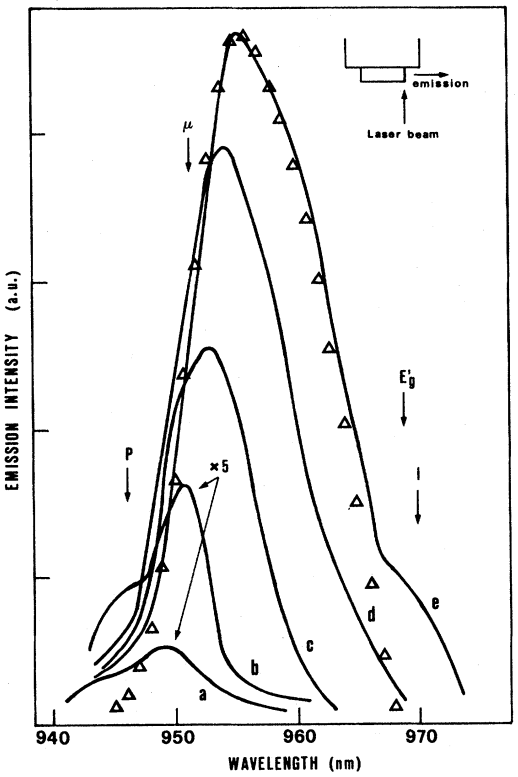

FIG. 4. Stimulated emission spectra (X line) of InSe at 20 K under sample edge dye laser excitation: curve a 40 kW/cm^2, curve b 80 kW/cm^2, curve c 0.8 MW/cm^2, curve d 1.6 MW/cm^2, and curve e 4 MW/cm^2. The triangles show a theoretical fitting; the position of P and I lines, of the chemical potential μ and of the reduced gap E_g' of the electron-hole plasma are shown by arrows.

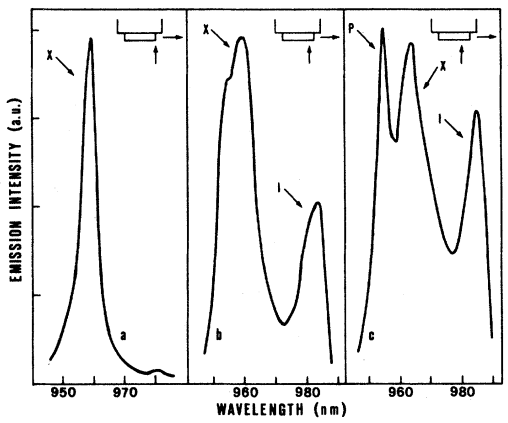

FIG. 5. Stimulated emission spectra of InSe at 90 K under dye laser excitation (2.5 MW/cm^2) at different values of the distance l from the sample edge: (a) $l=0$, (b) $l=20$ μm, and (c) $l=50$ μm.

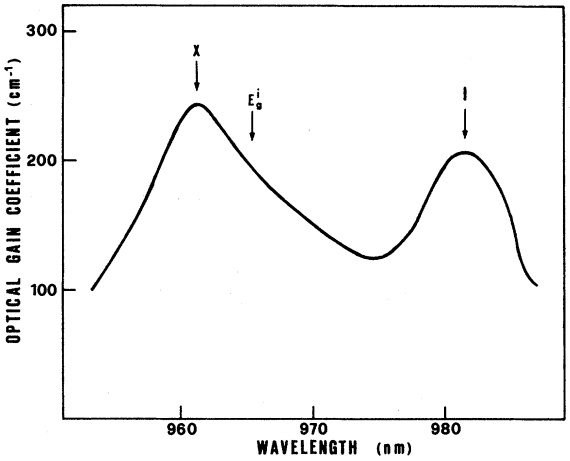

FIG. 6. Optical gain spectrum at 4 MW/cm^2 dye laser excitation in the pumping arrangement of Fig. 5(c). The arrows show the positions of E_g^i and of X and I lines.

dence of the last process should be as $I^{3/2}$. Moreover, according to the model by Fischer and Bille,[10] the emission peak due to exciton-carrier scattering should be at 32 meV below FE and its thermal shift should be linear with kT. Therefore the exciton-carrier scattering does not agree with our experimental data.

The quadratic dependence on FE and the thermal dependence we observed are better consistent with an exciton-exciton scattering process. For such collision the emitted photon energy is given by $h\nu=E_g-2E_{ex}^b-\Delta E$, where ΔE is the band filling term, a function of HED level like $I_0^{3/2}$. Therefore the energy difference between FE and P line is $E_{ex}^b+\Delta E$. We find this difference to be about 19 meV; this, for $E_{ex}^b=14.5$ meV, gives for ΔE a value of about 5 meV, well consistent with our HED levels.

With regard to the P' line of Fig. 3, we assume that the amplification channel is associated to a phonon replica of FE line, since the optical gain of the P' line is lower than the P line's one and, mainly, its separation in energy from FE corresponds exactly to the A_1' phonon of InSe ($h\nu_{ph}=14$ meV).[11]

On the contrary, the X line cannot be due to excitonic cooperative processes, because of its position in energy and the observed kinetics and broadening with temperature and HED level.

We ascribe this X band to the recombination of an electron-hole plasma (EHP) associated with the direct gap. The no-phonon EHP radiative recombination band can be theoretically fitted by[12]

$$I(h\nu)=I_0\int_0^{h\bar{\nu}} D_e(E)D_h(h\bar{\nu}-E)f(E,F_e,T) \times f(h\bar{\nu}-E,F_h,T)dE \ ,$$

where $F_{e(h)}$, $D_{e(h)}$, and f are the Fermi energy, the density of states, and the Fermi function for electrons (holes); $h\bar{\nu}=h\nu-E_g'$, being E_g' the reduced gap, associated with EHP, whose value can be obtained from experimental data, since it is the abscissa of the zero intensity point of the extrapolated low energy tail of the no-phonon EHP emission band. The density-of-state masses m_e and m_h for electrons and holes of Ref. 1 have been assumed.

We have considered negligible any "camel's-back" effects[13] on the conduction minimum. The EHP temperature has been considered to be the same of the bulk; then only $F=F_e+F_h$, i.e., the electron-hole pairs density, remains the fitting parameter to be adjusted. In this way we obtain a good fit for our experimental data between 20 and 90 K. A typical example is shown in Fig. 4, with $n_c=4\times10^{18}$ pairs/cm^3. From the fit values it is possible to estimate the binding energy of the plasma Φ compared to the exciton energy E_{ex}; being $\Phi=E_{ex}-(E_g'+F)$, we obtain for Φ a value of about 20 meV in InSe.

At high levels of HED we observe the I line, that shows optical amplification. If the excited region has a distance $l=0$ from the sample edge, this I line weakly appears, 23 meV below E_g^i, on the low-energy tail of the X line, that has a relatively much greater optical gain. But if the distance l is increased up to some tenths of microns the X line intensity strongly decreases because of self-absorption and the I line becomes comparable with the X line.

It is difficult to assign the nature of the process responsible for I-line emission; in fact, reliable values for indirect exciton binding energy and for the effective masses associated to the K minimum of the conduction band are not reported in literature. Nevertheless, we observe that the functional dependences of the I line on I_0 and T are similar to those of the P line and its emission is not strongly localized to the excited region, but it is associated with a diffusion mechanism of photoinjected carriers. Therefore we tentatively assume that I-line emission is due to an Auger process between a direct and an indirect exciton, as proposed for GaSe.[14] This assumption would be consistent with the stimulation effect, provided that the binding energy of the indirect exciton is of about 50 meV, i.e., larger than the one of the direct exciton, and then the effective electron mass in K point is larger than in Γ. Therefore the optical properties of InSe at its indirect edge should be known better, to get our assumption confirmed.

Concluding, we have investigated the highly photoexcited luminescence from InSe in the temperature range 20–300 K. Four different stimulated emission have been detected in this indirect-gap semiconductor. The optical gain spectrum and the strong external quantum efficiency of the various optical amplification process have been measured giving evidence of the practical interest for this material as a coherent near-infrared emitter.

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