APPLIED PHYSICS LETTERS **89**, 032108 (2006)

Optical spin injection in $CuGaSe_2/GaAs$ films

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(Received 3 April 2006; accepted 27 May 2006; published online 20 July 2006)

We have investigated polarization-resolved photoluminescence in epitaxially grown $CuGaSe_2/GaAs(001)$ films. Spin-polarized excitons are optically excited both below and above the characteristic crystal field splitting of the chalcopyrite. At low temperatures, a large exciton spin polarization of 35% is measured under resonant pumping but this is reduced by an order of magnitude and reverses its sign for nonresonant excitation. The measurements suggest that optical pumping within a small energy window just above the band gap results in the preferential generation of light holes and electrons that exhibit a long spin relaxation time, comparable to the recombination time in $CuGaSe_2$. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2233684]

There is considerable interest in the spin degree of freedom of carriers in the emerging field of spintronics but the realization of practical spintronic devices depends on efficient injection, transport, and detection of spin-polarized carriers. Thus, it is of interest to study materials where a high spin polarization can be realized. $CuGaSe_2$, a member of the chalcopyrite family, is a promising candidate. It is a direct band gap semiconductor (band gap energy $E_g = 1.731$ eV at $T = 10$ K) with applications in optoelectronics technology, for example, red-light-emitting diodes, light detectors, and solar cell devices. In this letter we report on polarization-resolved photoluminescence experiments on $GuGaSe_2$ films grown on GaAs substrates to evaluate the potential of this material for spintronic applications.

In optical pumping experiments on bulk zinc-blende materials [Fig. 1(a)], the radiative selection rules allow a population of spin-polarized electrons and holes to be excited by circularly polarized light. Due to the degeneracy of the heavy hole (hh) and light hole (lh) bands at the center of the Brillouin zone and the 3:1 relative strength of the hh/lh transitions, the maximum optical polarization that can be emitted, P_{circ}, is limited to 25%, corresponding to a maximum spin injected polarization P_{spin} of 50%.[1] In strained GaAs films, an internal crystal field is generated that lifts the degeneracy of the valence band so that in principle a 100% spin-polarized electron population can be photogenerated. Strain can be induced by growing on lattice mismatched substrates but this reduces the crystal quality and limits the achievable film thickness. Thick films usually exhibit a high dislocation density and poor optical properties.

By contrast most chalcopyrites (I-III-VI_2-compounds) and pnictides [2] have an internal crystal field splitting Δcf, which results in an energy splitting of the lh and hh bands at the center of the Brillouin zone. Lifting of the valence band degeneracy allows, in principle, the optical injection of 100% spin-polarized carriers, corresponding to emission of 100% circular polarized light[1] ($P_{\mathrm{spin}} = P_{\mathrm{circ}}$). Figure 1(b) shows the schematic band structure of one widely investigated member of the chalcopyrite family, $CuGaSe_2$. This material exhibits a negative Δcf splitting such that the center of the light hole band lies ~95 meV (Ref. 3) above the heavy hole band but strongly depends on the [Ga]/[Cu] film ratio. This ratio can be varied without losing the chalcopyrite phase but it is not easy to stabilize, since the film surface tends to be Cu deficient.[4] At higher energies the two bands cross and hybridization of the wave functions leads to mixing of the hole states. Thus, excitation of 100% spin-polarized carriers occurs only within a small energy window near the band gap energy. With decreasing Cu content the material band edge becomes less well defined[5] and this also leads to an increased intermixing of the lh and hh states.

The $CuGaSe_2$ films studied here are 400 nm thick and grown on GaAs(001) substrates by metal organic chemical vapor deposition (MOCVD). Electron channeling and trans-

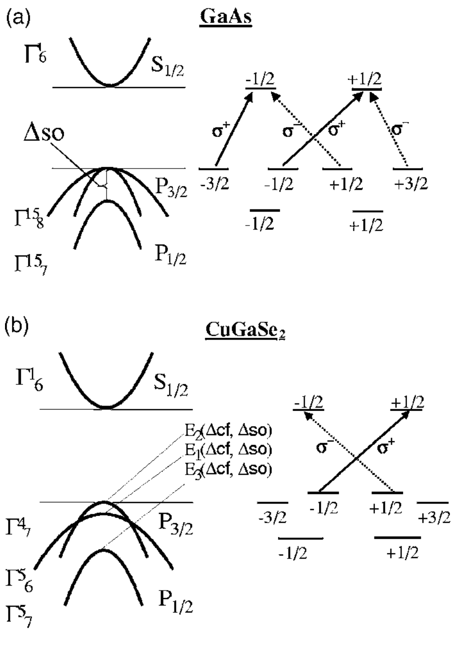

FIG. 1. (a) Band structure of GaAs and optical selection rules of excitonic recombination for excitation below the spin-orbit split band. (b) Band structure of $CuGaSe_2$ and optical selection rules of excitonic recombination for excitation below the crystal field splitting.

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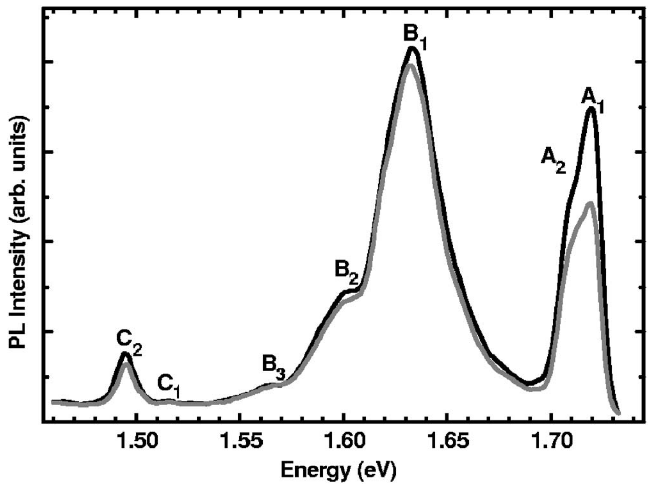

FIG. 2. Polarization-resolved photoluminescence at 15 K from the $CuGaSe_2/GaAs$ films. The black line represents the circular polarized PL component with the same sign as that of the polarizing laser beam (positive polarization), while the gray line that with the opposite sign (negative polarization).

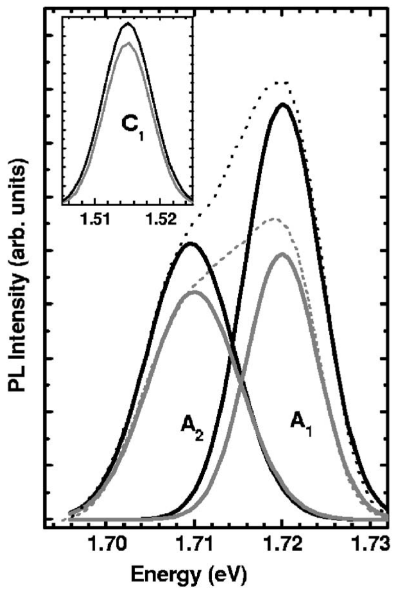

FIG. 3. PL circular polarized components in the vicinity of the $CuGaSe_2$ exciton under resonant excitation (1.75 eV). Black lines indicate a positive polarization while gray lines a negative one. Solid lines represent the results of the line shape fitting while dotted/dash lines the raw PL polarized data. In the inset the polarized PL components of the GaAs bulk exciton are displayed.

mission electron microscopy (TEM) measurements[6] have shown that the epilayers exhibit almost perfect epitaxial growth with oriented growth in the *c* direction of the tetragonal chalcopyrite structure. Since there is only a slight Cu excess during growth, nearly ideal stoichiometric films were produced that resulted in large values of Δcf. The samples were resonantly excited by a continuous wave Ti:sapphire laser (1.46–1.77 eV) pumped by a solid-state (2.33 eV) laser and nonresonantly excited by a He–Ne laser (1.958 eV). A combination of achromatic quarter wave plates and linear polarizers was used to generate circularly polarized laser light and analyze the emitted photoluminescence (PL).

The low-temperature ($T = 15$ K) optical pumping spectra under resonant excitation (1.75 eV, 15 mW) are shown in Fig. 2. The observed PL features are typical for $CuGaSe_2$ films grown under slight Cu excess by MOCVD.[7,8] The sharp features A_1 at 1.718 eV and A_2 at 1.712 eV are identified as the ground state $CuGaSe_2$ free exciton and acceptor bound exciton, respectively; the shallow acceptor state is a copper vacancy defect that is known to be responsible for the *p*-type nature of the material. Feature B_1 is a donor to copper vacancy acceptor transition with features B_2 and B_3 identified as the 1-LO and 2-LO phonon replicas of the B_1 transition. Features C_1 and C_2 are associated with the GaAs substrate, attributed to the free GaAs exciton (1.515 eV) and the conduction band to carbon acceptor transition (1.494 eV), respectively. Since the $CuGaSe_2$ films are excited just above the gap only light holes are generated and a high free exciton circular polarization is obtained. The circular polarization is defined as $P_{\text{circ}} = (I_+ - I_-)/(I_+ + I_-)$ where $I_+(I_-)$ are the intensities of the circularly polarized PL components with the same (opposite) sign as that of the polarized laser beam. By line shape fitting of the excitonic emission as seen in Fig. 3, an optical polarization P_{circ} of $(26.2 \pm 9)\%$ is obtained for the free exciton (feature A_1) with the sign of the polarization being the same as that of the laser exciting beam. This value must be modified to take account of the circular polarization of the laser beam P_L which was measured to be $(75 \pm 1)\%$ [this is because the laser energy (1.75 eV) lies at the end of the operating range of the quarter wave plate used]. We then deduce an optical polarization for the free exciton, $P_{\text{exc}} = P_{\text{circ}}/P_L$ of $(35 \pm 12)\%$. According to the radiative selection rules this is then equal to the injected steady-state exciton spin polarization in the $CuGaSe_2$ film. For the low excitation densities used here, the number of photogenerated spin-oriented holes is comparable to the intrinsic (unpolarized) hole population. Hole spins generally relax faster than electron spins, so the exciton spin polarization of 35% is effectively a measure of the optically injected electron spin polarization.

The relatively large error in the polarization measurement (±12%) is due to variations of the polarization as the laser spot was scanned across the sample. We attribute these variations to compositional fluctuations of the [Ga]/[Cu] film ratio, that would strongly affect the magnitude of the crystal field splitting. $CuGaSe_2$ films commonly exhibit spatially inhomogeneous luminescence; better control of the growth parameters would lead to greater film homogeneity and thus smaller fluctuations of the polarization signal.

The measured spin polarization is high but well below the predicted value (100%). The polarization loss could be due to electron spin relaxation during the exciton lifetime and/or partial intermixing of the light and heavy hole states within the crystal field splitting Δcf. In any case, the observation of a high optical polarization indicates a long electron spin lifetime under resonant excitation, comparable to the recombination of $CuGaSe_2$.[9] The acceptor bound exciton (feature A_2) exhibits a circular polarization of $P_{\text{bexc}} = (11.2 \pm 5)\%$, three times smaller than that of the free exciton. This is attributed to the more complicated recombination processes that involve the impurity center and during which there is a larger possibility for an electron spin-flip to occur. We note here that the only accurate way to correctly obtain the spin injection efficiency is to spectroscopically resolve and deduce the optical polarization of the free excitonic transition.[10]

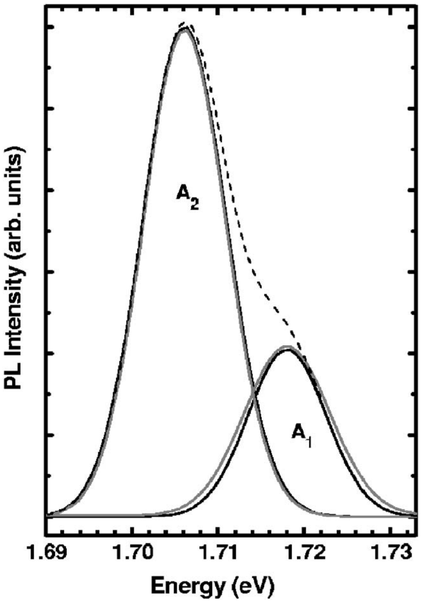

FIG. 4. PL circular polarized components in the vicinity of the $CuGaSe_2$ exciton under nonresonant excitation (1.958 eV). Black lines indicate a positive polarization while gray lines a negative one. Solid lines represent the results of the line shape fitting while dotted lines the raw unpolarized PL.

The inset of Fig. 3 shows the two circularly polarized components of the free GaAs exciton (feature C_1) for excitation at 1.75 eV. At this energy the penetration depth of the laser is greater than 400 nm. The optical polarization of the feature is $(9.7\pm1.5)\%$ which is approximately four times smaller than the polarization of the free exciton in the $CuGaSe_2$ film. Such a reduction is theoretically expected[1] for a semiconductor with degenerate heavy and light holes (GaAs) relative to the polarization observed in a semiconductor with nondegenerate hole bands ($CuGaSe_2$) when excited under the same pumping conditions. This confirms that excitation below the crystal field splitting of the $CuGaSe_2$ preferentially populates the light hole bands and indicates that at the particular excitation energy the light/heavy hole band intermixing is small.

Figure 4 shows the polarized PL in the vicinity of the $CuGaSe_2$ exciton for excitation at 1.958 eV; above the light and heavy hole bands but slightly below the spin-orbit split hole band[11,12] ($E_g+\Delta\approx1.97$ eV). As the films have their c axis oriented perpendicular to the substrate plane, our experimental configuration allows transitions to all hole bands.[12] Line shape analysis now shows the excitonic emission to be dominated by the bound exciton feature A_2. He–Ne light has a smaller penetration depth into the sample and this is confirmed by the absence of GaAs substrate emission. In addition it might be expected that the contribution to the PL signal close to the film surface will be enhanced. Since this region tends to be Cu deficient,[4] there will be a larger density of copper vacancy defects (acceptors) here and this will result in a greater bound exciton contribution.

The polarized PL data show a dramatic reduction of the circular polarization of both the free (A_1) and the acceptor bound exciton (A_2) transitions when compared with the resonantly excited spectra. Importantly the circular polarization of the free exciton changes sign, showing a small but consistent negative polarization of $P_{\text{spin}}=P_{\text{circ}}=(-3.5\pm2.5)\%$; here the minus sign indicates that the polarization is opposite to that of the exciting laser beam. These results can be understood using the following arguments: if we assume, without any loss of generality, that the polarization of the laser line is σ_+, then according to the selection rules (Fig. 1) the laser excites the $-\frac{1}{2}$ lh to $+\frac{1}{2}$ e as well as the $-\frac{3}{2}$ hh to $-\frac{1}{2}$ e excitonic transitions. Since there is no PL signature of the heavy hole exciton we assume that the photogenerated $-\frac{3}{2}$ heavy hole rapidly relax to the $\pm\frac{1}{2}$ light hole band. Taking into account that heavy hole transitions are more probable than those of light holes as observed in photoreflectance measurements,[12] we are then left with approximately equal numbers of holes in the $\pm\frac{1}{2}$ light hole states but with more $-\frac{1}{2}$ than $+\frac{1}{2}$ electrons. The excess of $-\frac{1}{2}$ electrons results in light hole exciton emission of σ_- polarized light, i.e., light with polarization opposite to that of the exciting laser beam (negative polarization).

The change in sign of the free exciton polarization cannot be explained in terms of spin loss during exciton thermalization. Relaxation of hot electron/hole pairs is known to result in partial loss of the spin information by the Dyakonov-Perel mechanism[1] but should not lead to a change of sign of the overall PL polarization when only heavy and light holes are populated. Instead the transition from a large positive to a small negative polarization is indicative of population of different valence band states as the PL excitation energy varies below and above the crystal field splitting of $CuGaSe_2$.

In summary, we have performed a polarization-resolved luminescence study of epitaxial $CuGaSe_2$ films on GaAs substrates. Hole excitation below the characteristic crystal field splitting results in a high steady-state free exciton spin polarization, substantially larger than the 25% limit expected for degenerate hh/lh bands, indicating that light holes are preferentially generated. Comparison of the optical polarization of the $CuGaSe_2$ and GaAs excitons and nonresonant laser excitation further support this argument. These measurements indicate a relatively large $CuGaSe_2$ electron spin lifetime. Further work is under way to investigate in detail the spin relaxation mechanisms in $CuGaSe_2$ and quantify the spin lifetime.

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