BRIEF NOTE

Excited States of the A and B Free Excitons in CuInSe$_2$

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CuInSe$_2$ single crystals, grown by the vertical Bridgman technique were studied using polarisation resolved photoluminescence (PL) at cryogenic temperatures. The emission lines related to the first ($n = 2$) excited states for the A and B free excitons were observed in the PL spectra at 1.0481 and 1.0516 eV, respectively. The spectral positions of these lines were used to estimate accurate values for the A and B exciton binding energies (8.5 and 8.4 meV, respectively), Bohr radii (7.5 nm), band gaps ($E_g^A = 1.050$ eV and $E_g^B = 1.054$ eV), and the static dielectric constant (11.3) assuming the hydrogenic model. © 2011 The Japan Society of Applied Physics

CuInSe$_2$-based solar cells are currently demonstrating the leading performance amongst thin-film technologies: 20%[1] conversion efficiency and excellent stability. CuInSe$_2$ is a semiconductor with direct band gap near 1.05 eV and an absorption coefficient exceeding 10^5 cm^{-1}. Despite a considerable amount of research fundamental understanding of the material is still low and does not match its importance.

A key milestone in the understanding of every semiconductor material is the observation of free excitons and their excited states. Their spectral positions offer a reliable way to accurately determine the free exciton binding energies E_b and the band gap E_g. Despite many studies of the optical properties of CuInSe$_2$ dating back nearly 40 years[2] only very few reports suggest resolution of the A and B excitonic states.[3–5] No reliable information on their excited states has yet been reported. Determining E_b from the spectral positions of the photoluminescence (PL) lines of the free exciton ground and excited states does not involve any other material parameters providing an opportunity to clarify the static dielectric constant ε, which also reveals a considerable scatter in the literature (from 9.3[6] to 16[7]), assuming published values of the effective masses are correct and the validity of the hydrogenic model.

In this report PL and optical reflectance (OR) data on CuInSe$_2$ single crystals are used to resolve the A and B free excitons and their excited states. To probe the symmetry and clarify the assignments polarisation resolved PL spectra are used. The spectral positions of the PL lines related to excited states helped to calculate accurate values of the static dielectric constant as well as E_g, E_b, and Bohr radii of the A and B free excitons in CuInSe$_2$.

Bulk single crystals of CuInSe$_2$ were cleaved from an ingot grown by the vertical Bridgman technique.[8] The elemental composition of the crystals, measured by energy dispersive X-ray analysis (EDX) was close to ideal stoichiometry (Cu: 24.9, In: 24.9, and Se: 50.2 at. %). The orientation of the three major cubic structure crystallographic axes ⟨001⟩, ⟨010⟩, and ⟨100⟩ of the samples was established by analysis of X-ray Laue patterns. Cleaved surfaces of the crystal were examined using PL and OR at 6 K in Strathclyde and at 4.2 K in the Grenoble High Magnetic Field Laboratory (GHMFL). The PL measurements employed the unpolarised 514 nm line of an Ar$^+$ laser
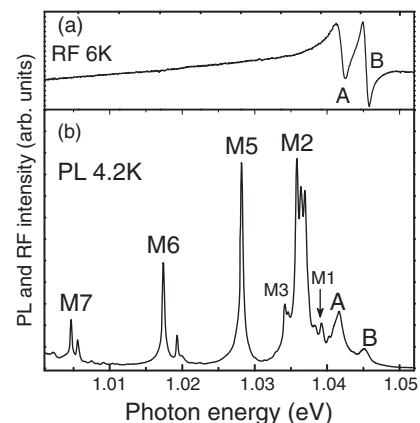

Fig. 1. The OR (a) and PL (b) spectra for CuInSe$_2$ single crystals taken at 6 and 4.2 K, respectively, showing lines of free and bound excitons.

as an excitation source whilst the OR measurements used a 100 W tungsten halogen lamp. The spectral resolution was determined as 0.07 meV for the RF, 0.8 meV for the polarisation resolved PL at 6.5 K, and 0.14 meV for the PL at 4.2 K. The spectral position of the lines was determined with an accuracy of 0.2 meV.

The near band gap region of the PL and OR spectra taken in CuInSe$_2$ at 4.2 and 6 K, respectively, using non-polarised light, are shown in Figs. 1(a) and 1(b), respectively. The OR spectrum reveals two prominent resonances, associated with the A and B free excitons, confirming that the lines at 1.0417 and 1.0453 eV in the PL spectra are related to the A and B free excitons.[4,5] The spectrum also shows several well resolved lines M1–M7 which have been previously attributed to bound excitons and their excited states.[4,5]

The chalcopyrite structure of CuInSe$_2$ can be derived from the sphalerite zincblende structure of ZnSe by replacing Zn either with Cu or In. The two non-equivalent replacements result in different lengths for the chemical bonds Cu–Se and In–Se creating a tetragonal distortion[9] which splits the triply degenerated valence band in ZnSe into the three sub-bands A, B, and C. The region of the free excitonic transitions is examined more closely using PL spectra measured with a linear polariser oriented either along ($E \parallel c$) or perpendicular ($E \perp c$) to the c-axis of the crystalline lattice as shown in Fig. 2(a). The A free exciton emission is predominantly polarised $E \perp c$, reaching a

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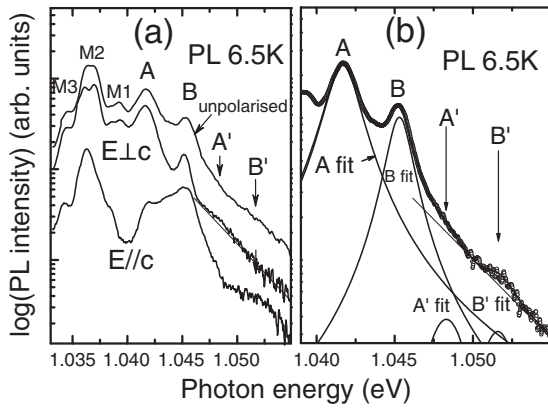
Fig. 2. The PL spectra for CuInSe$_2$ single crystals: (a) taken at polarised $E \perp c$, $E \parallel c$, and unpolarised conditions (offset for clarity); (b) unpolarised PL spectra fitted with A, B, A′, and B′ Lorentzians.

Table I. The band gap E_g, binding energies E_b, and Bohr radii a_B of the A and B excitons in CuInSe$_2$.

Exciton	E_b (meV)	a_B (nm)	E_g (eV)
A	8.5	7.5	1.0502
B	8.4	7.5	1.0537

maximum intensity $I_\perp^A$ at this polarisation. This is consistent with the selection rules for an A excitonic transition involving the Γ_{6v} symmetry of the top valence sub-band and the Γ_{6c} symmetry of the conduction band. According to the quasi-cubic model,[10] the theoretical ratio of $I_\perp^A/I_\parallel^A$ intensities should reach 9.[11] In our PL experiment the value of $I_\perp^A/I_\parallel^A$ is 7.1, approaching the theoretical value more closely than the earlier reported value of 5 for electro-reflectance.[11] The B exciton line intensity is almost unchanged with polarisation, which is consistent with the selection rules for a transition between the Γ_{7v} symmetry B valence sub-band and the Γ_{6c} symmetry conduction band for both the $E \perp c$ and $E \parallel c$ polarisations.[11] Its width however is reduced from about 2.2 meV (non-polarised) to 1.1 meV ($E \perp c$ polarisation). For the $E \parallel c$ polarisation the reduced strength of the A exciton ground and excited transitions improves the visibility of the excited state line of the B exciton and also clarifies the A′ ($n = 2$) contribution to the high-energy tail of the B exciton line. For the $E \perp c$ polarisation the narrowing of the B exciton line allows the line related to the A′ excited state, to be resolved as shown in Fig. 2(a). The straight line emphasises its presence. The excited state lines can also be seen in the unpolarised PL spectra taken at higher excitation density as shown in Fig. 2(b). The B exciton excited state B′ is clearly resolved, whereas A′ is not resolved due to the proximity of the B line. In order to determine the spectral positions this unpolarised PL spectrum has been fitted with Lorentz shape curves of A, B, A′, and B′. The spectral positions of the excited states A′ and B′ were found to be 1.0481 and 1.0516 eV, respectively. According to the hydrogenic model for simple parabolic bands in a direct bandgap material the spectral position $E(n)$ of a free exciton line in the nth excited state is[12]

$$E(n) = E_g - E_b = E_g - 13.6 \frac{\mu}{m_0 \varepsilon^2 n^2}, \qquad (1)$$

where $\mu = m_e m_h / (m_e + m_h)$ is the reduced mass of exciton, m_0 is the free electron mass, m_e is an effective electron and

m_h an effective hole masses, and ε is the static dielectric constant of the material. From the spectral separation of the ground $E(n = 1)$ and excited $E(n = 2)$ states, the binding energies of the A and B excitons were calculated as $E_b = 4[E(n = 2) - E(n = 1)]/3$ and are shown in Table I. Accurate values of the A and B band gaps are also calculated as $E_g = E(n = 1) + E_b$ and shown in Table I. Assuming literature values of the effective masses for the electron and hole in CuInSe$_2$ ($m_e = 0.09 m_0$ and $m_h = 0.71 m_0$, respectively[13]), the static dielectric constant in CuInSe$_2$ was calculated using eq. (1) $\varepsilon = 11.3$. The Bohr radii a_B for the A and B free excitons were calculated as $a_B = a_B^H m_0 \varepsilon / \mu$, where a_B^H is the Bohr radius for hydrogen, and are shown in Table I.

In conclusion, high quality CuInSe$_2$ single crystals were studied by OR and PL spectroscopy, employing polarisation dependence to clarify the properties of the free exciton transitions. The lines related to the first ($n = 2$) excited states for the A and B free excitons at $E_A(n = 2) = 1.0481$ and $E_B(n = 2) = 1.0516$ eV, respectively, have been observed in the PL spectra. Accurate values of the A and B exciton binding energies $E_b^A = 8.5$ and $E_b^B = 8.4$ meV have been established and used to estimate Bohr radii of 7.5 nm for both excitons, 6 K band gap of 1.050 eV for the A-exciton and of 1.054 eV for the B-exciton as well as the value of 11.3 for the static dielectric constant. A standard hydrogenic model is assumed.

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