Transactions of the Materials Research Society of Japan. Vol. 20

Second-harmonic generation in $CuInSe_2$ and $CuGaSe_2$ thin films on GaAs(001)

D. J. Bottomley[a], A. Mito[b], S. Niki[a] and A. Yamada[a]

[a]Electrotechnical Laboratory, 1-1-4 Umezono, Tsukuba-shi, Ibaraki-ken, Japan 305.

[b]National Research Laboratory of Metrology, 1-1-4 Umezono, Tsukuba-shi, Ibaraki-ken, Japan 305.

We investigate the second order nonlinear optical (NLO) properties of chalcopyrite-structure $CuInSe_2$ and $CuGaSe_2$ thin films grown on GaAs(001) using optical second-harmonic (SH) generation at a fundamental wavelength of 790 nm. The SH intensities yielded by approximately stoichiometric $CuInSe_2$ and $CuGaSe_2$ thin films are similar to that of GaAs. The second order optical nonlinearities are strongly curtailed in non-stoichiometric thin films. Our observations support our proposal that thin films of tetragonal chalcopyrite-structure semiconductor media are promising NLO materials for the following reasons: phase-matching is possible in them in principle; they can be utilized in a waveguide geometry, and they are compatible with III-V substrates.

1. INTRODUCTION

Recently, thin films of tetragonal chalcopyrite semiconductors have been put forward as being potentially useful in nonlinear optics (NLO) [1]. This crystal class includes $AgGaS_2$ and $AgGaSe_2$, which have been applied in bulk form as NLO materials in long wavelength (2 to 20 μm) optical parametric oscillators [2, 3]. The structure of chalcopyrite compounds is shown in Fig. 1. The ratio of the c-axis to a-axis lattice constants in these crystals, c/a, is always approximately 2. We investigate the second order NLO properties of $CuInSe_2$ and $CuGaSe_2$ thin films grown on GaAs(001). The a-axis strains of these materials when grown coherently on GaAs(001) are relatively small at -2.2% and +0.7%, respectively; their bulk bandgaps (which are direct) are 1.04 eV and 1.68 eV, respectively [4]. We will focus on two issues: the size of the optical nonlinearity of these media in thin film form and its dependence on the material stoichiometry. The latter consideration is important in that the use of three atomic beams for growth makes achieving near-perfect stoichiometry difficult.

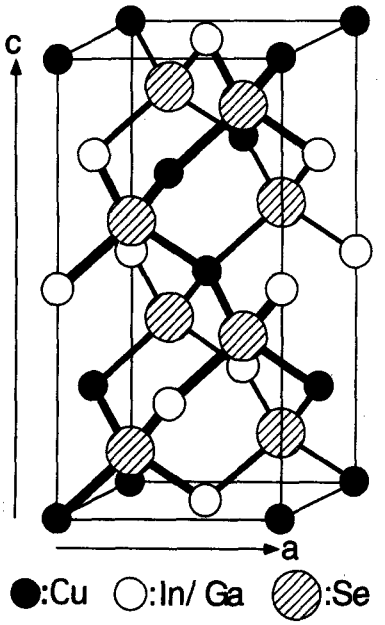

Fig. 1 The chalcopyrite structure.

2. THEORY AND EXPERIMENT

The chalcopyrite thin films investigated here were $0.8 \pm 0.2 \mu m$ thick and were grown on

GaAs(001) by molecular beam epitaxy in a system described elsewhere [5]. The films were relaxed *i.e.* not strained. X-ray diffraction showed that the films' c-axes were parallel to [001] [6]; their stoichiometries were determined using an electron probe for microanalysis. Table 1 lists the stoichiometries of the samples investigated. The second order NLO properties were investigated using second harmonic generation (SHG) performed in reflection at an angle of incidence of 45°, at a fundamental wavelength of 790 nm using a Ti:sapphire laser with a pulse width of 100 fs, a repetition rate of 100 MHz and a time-averaged power of 400 mW. The refractive indicies $n(\omega)$ at the fundamental and second harmonic (SH) frequencies of the thin films alone (excluding the substrate) were measured using ellipsometry at a 75° angle of incidence. The difference in the above angles of incidence contributes negligibly to the error in the measured values of the second order NLO susceptibility tensor $\chi_{ij}^{(2)}$ because this error is dominated by the possibility of surface contributions, discussed below.

The NLO experimental wavelength was chosen to simplify interpretation of the SHG data: as discussed below, the absorption in the films at the SH wavelength is sufficiently strong that the substrate does not contribute to the measured SH response. In addition, the absorption at the fundamental wavelength is such that multiple internal reflections do not occur within the film; van Hasselt *et al.* have shown that these complicate data interpretation [7]. The information gleaned from our experiments can be applied to optimize $\chi_{ij}^{(2)}$ for the more practical sub-bandgap wavelengths.

The SH intensity $I_{g,h}^{(2\omega)}$ was measured for s and p fundamental polarizations g and for s and p SH polarizations h as a function of sample azimuthal angle ψ for all samples listed in Table 1, as well as from a GaAs(001) wafer. The data was fitted with the following functions [8]:

$$I_{g,p}^{(2\omega)}(\psi) \propto \left|A + B\cos(2\psi)\right|^2 \tag{1}$$

$$I_{p,s}^{(2\omega)}(\psi) \propto \left|B\sin(2\psi)\right|^2 \tag{2}$$

and the values of the coefficients A and B were derived. Note that B can arise from both interfacial and bulk sources, whereas A can arise solely from interfacial sources [8]. Figure 2 shows $I_{p,s}^{(2\omega)}(\psi)$ from approximately stoichiometric thin films of $CuInSe_2$ and $CuGaSe_2$ as well as from GaAs(001). It is clear that of these samples, the $CuGaSe_2$ thin film yields the largest $I_{p,s}^{(2\omega)}$.

In bulk form, $CuInSe_2$ and $CuGaSe_2$ are tetragonal and have the point group $\bar{4}2m$ implying they have two independent elements of $\chi_{ij}^{(2)}$ [9]. The SH field from bulk sources $E_{g,h}^{(2\omega)}$ has the following dependence on ψ for rotation about [001]:

$$E_{p,s}^{(2\omega)}(\psi) \propto 2\chi_{14}^{(2)} f_c f_s \sin(2\psi) \tag{3}$$

$$E_{s,p}^{(2\omega)}(\psi) \propto \chi_{36}^{(2)} F_s \cos(2\psi) \tag{4}$$

Table 1. Compositions and the Linear and SHG Properties of the Nominally $CuInSe_2$ and $CuGaSe_2$ Thin Films

Sample No.	Composition (at. %)[a] Cu	In	Ga	Se	$n(\omega)$	$n(2\omega)$	$\lvert\chi_{14}^{(2)}\rvert$[b]	$\lvert\chi_{36}^{(2)}\rvert$[b]	The Larger $\lvert A/B\rvert$ for $I_{g,p}^{(2\omega)}$
CIS206	25.0	24.0	0	51.0	2.09 − *i*0.92	1.74 − *i*1.32	0.095	0.073	0.07
CIS207	20.0	27.5	0	52.5	2.67 − *i*0.68	2.09 − *i*1.20	0.050	0.059	0.41
CIS208	21.5	26.5	0	52.0	2.72 − *i*0.66	2.16 − *i*1.24	0.086	0.096	0.28
CGS145	29.0	0	22.0	49.0	2.40 − *i*0.92	1.56 − *i*1.25	0.10	0.033	0.19
CGS150	23.0	0	26.5	50.5	2.84 − *i*1.04	2.19 − *i*1.14	0.055	0.024	1.90
CGS265	25.0	0	24.5	50.5	3.02 − *i*0.22	2.46 − *i*1.48	0.29	0.14	0.06

[a] Composition values are given to within ±1 at. %.
[b] $\lvert\chi_{14}^{(2)}\rvert$ and $\lvert\chi_{36}^{(2)}\rvert$ are expressed relative to the $\lvert\chi_{14}^{(2)}\rvert$ of GaAs.

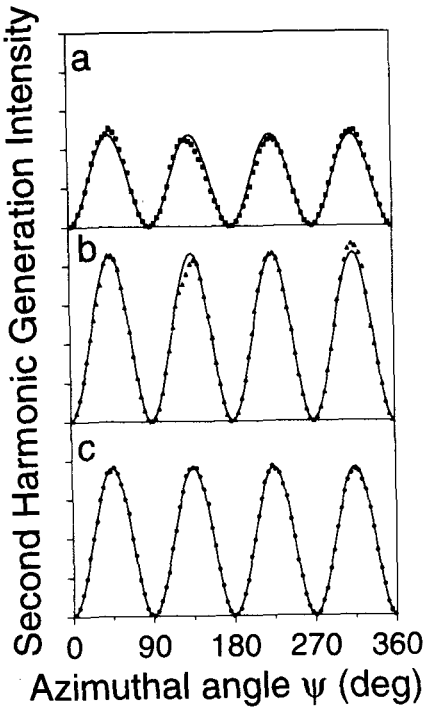

Fig. 2. $I_{p,s}^{(2\omega)}(\psi)$ from (a) a $CuInSe_2$ thin film (sample CIS206), (b) a $CuGaSe_2$ thin film (sample CGS265), and (c) GaAs(001). The data (points) are to scale; the curves are fits using relation (2).

$$E_{p,p}^{(2\omega)}(\psi) \propto (2\chi_{14}^{(2)} F_c f_c f_s - \chi_{36}^{(2)} F_s f_c^2)\cos(2\psi) \qquad (5)$$

where f_s, f_c, F_s and F_c are Fresnel factors [8]. The omitted constants of proportionality in Eqs. (3-5) are identical apart from polarization-dependent transmission coefficients. Assuming that the SH field with C_{2v} symmetry arises solely from the bulk, and using Eqs. (3-5), one can obtain $|\chi_{14}^{(2)}|$ and $|\chi_{36}^{(2)}|$ for each film relative to the $|\chi_{14}^{(2)}|$ of GaAs, when one corrects for linear effects. These values are given in Table 1, along with $n(\omega)$ and $n(2\omega)$. The phase difference between $\chi_{14}^{(2)}$ and $\chi_{36}^{(2)}$ was consistent with 0°. From the measured $\mathrm{Im}(n(2\omega))$ of the thin films, the SH absorption depth is typically ~ 25 nm. Therefore the buried interface and substrate are too deep to contribute to the observed $I_{g,h}^{(2\omega)}$: the A in Eq. (1) arises solely from surface sources, and the B in Eqs. (1) and (2) arises solely from the film and its surface. The fractional error in $|\chi_{14}^{(2)}|$ and $|\chi_{36}^{(2)}|$ due to surface contributions can be estimated from the larger value of $|A / B|$ in Eq. (1) for $I_{g,p}^{(2\omega)}$ (g = s or p) given in Table 1.

3. RESULTS AND DISCUSSION

We will now discuss the data reported in Table 1. The values of $|\chi_{14}^{(2)}|$ in approximately stoichiometric $CuInSe_2$ and $CuGaSe_2$ thin films are 0.095 and 0.29 that of GaAs, respectively. Typically, the values of the $|\chi_{ij}^{(2)}|$ decrease rapidly with departure from non-ideal stoichiometry: $|\chi_{ij}^{(2)}|$ is a stronger function of stoichiometry than the refractive index. In general in noncentrosymmetric media one would expect second order NLO effects to be more sensitive to defect generation than linear optical effects. The reason is that defects tend to lead to a centrosymmetric structure, the limiting case being that of an amorphous medium for which $\chi_{ij}^{(2)}$ vanishes. This expectation is consistent with the $|\chi_{ij}^{(2)}|$ values yielded by the approximately stoichiometric chalcopyrite thin films in that the material with the lower lattice mismatch to the substrate, $CuGaSe_2$, and hence with the lower density of misfit dislocations, yields the higher $|\chi_{ij}^{(2)}|$ values.

Non-stoichiometric $CuInSe_2$ samples have been shown to have a structure which differs from the ideal chalcopyrite structure in that it contains a sphalerite component [6, 10]. This is consistent with the data for samples CIS207 and CIS208 for which $|\chi_{14}^{(2)}|$ and $|\chi_{36}^{(2)}|$ are equal within the fractional error due to surface contributions, as in sphalerite compounds. In $CuInSe_2$ In-rich films, the antisite defect In_{Cu} is a candidate defect [5, 6, 10]. Owing to the larger radius of In compared to Cu, it is expected to lead to local crystal distortion, which would reduce $\chi_{ij}^{(2)}$ as observed for the In-rich film CIS207 in Table 1. Although film CIS208 is non-stoichiometric, its In concentration of 26.5 ± 1 at% is close to the stoichiometric value. Furthermore, its $|\chi_{ij}^{(2)}|$ values are similar to the stoichiometric film CIS206: this supports the

hypothesis that the In concentration has the greatest influence on the $|\chi_{ij}^{(2)}|$ values. Little is known of the defects in non-stoichiometric $CuGaSe_2$, but we expect effects similar to those in $CuInSe_2$ owing to the structural and chemical similarity of these compounds.

$|\chi_{14}^{(2)} / \chi_{36}^{(2)}|$ is approximately 2 for the $CuGaSe_2$ films, but only approximately 1 for the $CuInSe_2$ films. This is consistent with the behaviour of the tetragonal distortion $|2-c/a|$ which is larger at 0.04 in $CuGaSe_2$ than 0.01 in $CuInSe_2$ [4]. Hence one would expect a greater difference in the electronic structure between the [001] and [100] directions in $CuGaSe_2$ than in $CuInSe_2$. The values of the phase differences between $\chi_{14}^{(2)}$ and $\chi_{36}^{(2)}$ are consistent with a value of 0°: this result is not surprising because $\chi_{14}^{(2)}$ and $\chi_{36}^{(2)}$ arise from the same material [11].

4. CONCLUSIONS

The SH intensities yielded by approximately stoichiometric $CuInSe_2$ and $CuGaSe_2$ thin films are similar to that of GaAs. The second order optical nonlinearities are strongly curtailed in non-stoichiometric thin films. The former observation implies a promising future for thin films of chalcopyrite semiconductors as NLO materials; the latter observation will be important for investigating the NLO properties of thin films of other chalcopyrite semiconductors such as $AgGaS_2$ and $AgGaSe_2$.

ACKNOWLEDGEMENTS

D.B. acknowledges receipt of a Japanese Science and Technology Agency Fellowship. H. Yajima and H. Oyanagi are thanked for their support, as is P. Fons for sharing his computational expertise and enthusiasm.

REFERENCES

1. D. J. Bottomley, A. Mito, S. Niki, and A. Yamada, Opt. Lett. **21**, 254 (1996). D. J. Bottomley, A. Mito, S. Niki, and A. Yamada, Bull. Electrotech. Lab. **60**, 199 (1996).
2. M. M. Fejer, Phys. Today, **47**(5), 25 (1994).
3. G. C. Bhar, Jpn. J. Appl. Phys. **32**, Suppl. 32-3, 653 (1993).
4. O. Madelung, ed., Physics of Ternary Compounds, sub-vol. h of Vol. 17, Semiconductors, Landolt-Börnstein Numerical Data and Functional Relationships in Science and Technology (Springer-Verlag, Berlin, 1985).
5. S. Niki, Y. Makita, A. Yamada, O. Hellman, P. J. Fons, A. Obara, Y. Okada, R. Shioda, H. Oyanagi, T. Kurafuji, S. Chichibu, and H. Nakanishi, J. Cryst. Growth **150**, 1201 (1995).
6. Y. Okada, R. Shioda, S. Niki, A. Yamada, H. Oyanagi, and Y. Makita, presented at the Solid State Devices and Materials Conference, Yokohama, Japan, August 1994.
7. C. W. van Hasselt, M. A. C. Devillers, Th. Rasing, and O. A. Aktsipetrov, J. Opt. Soc. Am B **12**, 33 (1995).
8. X. H. Qu, D. J. Bottomley, H. Ruda and A. J. SpringThorpe, Phys. Rev. B **50**, 5703 (1994).
9. P. N. Butcher and D. Cotter, The Elements of Nonlinear Optics (Cambridge U. Press, Cambridge, 1990).
10. R. Shioda, Y. Okada, H. Oyanagi, S. Niki, A. Yamada, and Y. Makita, J. Cryst. Growth **150**, 1196 (1995).
11. E. Ghahramani, D. J. Moss, and J. E. Sipe, Phys. Rev. Lett. **64**, 2815 (1990).