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Epitaxial Growth of $AgGaSe_2$ for Mid-Infrared Frequency Doubling Applications

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1. Introduction

In 1972, the non-linear properties of silver-selenogallate ($AgGaSe_2$) were published and several applications were foreseen [1]. Fourteen years later the achievement of a broadly tunable infrared parametric oscillator based on this material was announced [2], a delay mainly due to the lack of reproducible synthesis of high quality bulk $AgGaSe_2$ [3] crystals. Now, nearly another fourteen years later, crystal quality improvements are still yielding more applications of this material as second, third and difference frequency harmonic generators, parametric oscillators and amplifiers (See the July 1998 issue of the MRS Bulletin dedicated to this material system and applications).

On the other hand, thin film optoelectronic and all-optical technologies are making more and more use of non-linear optical components which could benefit from this naturally suited birefringent material. A strongly birefringent waveguide made of such material as $AgGaSe_2$ does not require quasi-phase-matching techniques such as periodic phase reversal, which are often technologically challenging. If light is propagating normal to the optical axis, type I phase matching in the infrared is possible at 3.0 μm and 12.7 μm for $AgGaSe_2$[1]. Some tuning by temperature is possible and has been demonstrated for bulk crystals [4], while composition tuning is also in principle possible.

To the authors' knowledge, no success in the growth of epitaxial $AgGaSe_2$ has been reported in the literature. It was our goal to determine the feasibility of growth using molecular beam epitaxy (MBE) of optical quality $AgGaSe_2$ and to further probe its possible integration in a viable device.

At the time of this writing, as will be described shortly, we were able to show firstly that the chalcopyrite phase of $AgGaSe_2$ can indeed be grown by MBE, and secondly that on a properly lattice-matched substrate the optical axis can be made to align with the direction of growth. In this configuration, waveguides can in principle be made in which the light travels normal to the optical axis, as required by the birefringent phase-matching condition.

2. Experimental

The chalcopyrite unit cell is a tetragon with a short *a*-axis and a long (optical) *c*-axis, with $c/2 \cong a$. Fig 1 shows the bandgap energies versus the *a*-axis lattice constant of several chalcopyrite compounds, the *c*/2 axis of $AgGaSe_2$ and the lattice constant of some cubic substrates. Growths performed

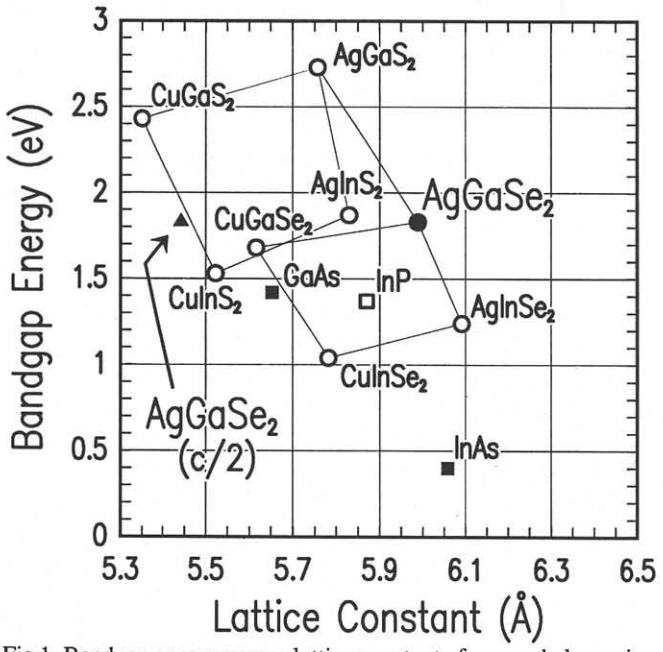

Fig 1. Bandgap energy versus lattice constant of some chalcopyrites (circles). Also shown is the *c*/2 lattice constant for $AgGaSe_2$ (triangle) as well as some standard substrates (squares).

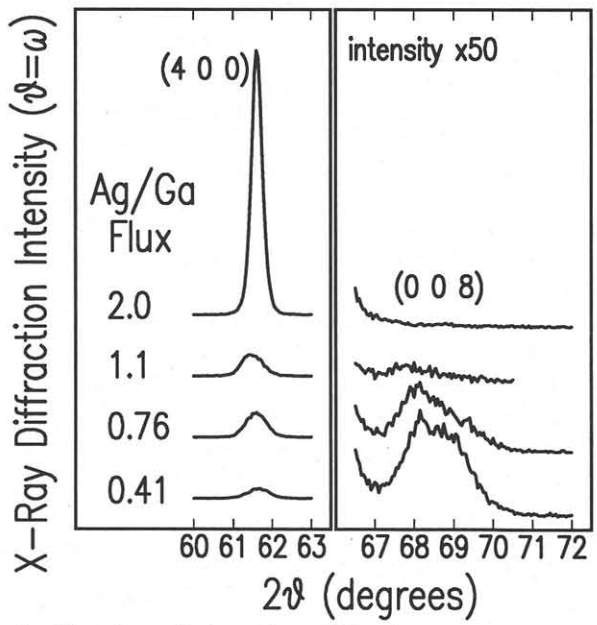

Fig 2. Growth on GaAs. X-ray diffraction spectra near angles corresponding to the chalcopyrite structure of $AgGaSe_2$ ((400) and (008) reflections for *a* and *c* axes respectively). Curves for samples grown at four different silver/gallium flux ratios are shown.

on both GaAs and InAs substrates are reported here.

The growth apparatus consists of a solid source MBE chamber with elemental silver, gallium and selenium sources heated to give nominal atomic flux ratios at the substrate of 1:1:100 respectively. The fluxes are measured prior to growth by an ion gauge placed at the sample location, and the values given in the following data are the uncorrected gauge readings (i.e. a Ag/Ga flux ratio of 1.0 does not necessarily correspond to a stoichiometric composition between silver and gallium). Growth temperatures were between 390°C and 500°C.

The samples were examined using standard x-ray diffraction methods for crystal quality and second phase analysis. Scanning electron microscopy and electron microprobe were used for overall as well as selective-area elemental composition measurement. Low temperature (1.5K) photoluminescence (PL) spectroscopy using a Fourier transform infrared spectrometer was also performed.

3. Results

Fig 2 and Fig 3 show data for samples grown on GaAs. In Fig 2, clear evidence that the chalcopyrite structure of $AgGaSe_2$ has been grown at the highest Ag/Ga flux ratio is seen, but the orientation of the optical *c*-axis is along the plane of the substrate (i.e. the *a*-axis is pointing up). Growth on InAs (Fig 4) also showed the chalcopyrite structure, but this time the optical axis was clearly grown normal to the surface.

The PL spectra in Fig 3 are for the same samples as those of Fig 2. The correspondingly best sample's spectrum (also determined to be near stoichiometry) is comparable to that of high quality grown material [5], while the "silver-poor" samples show a broad band which may signal the presence of the Ga_2Se_3 phase [6].

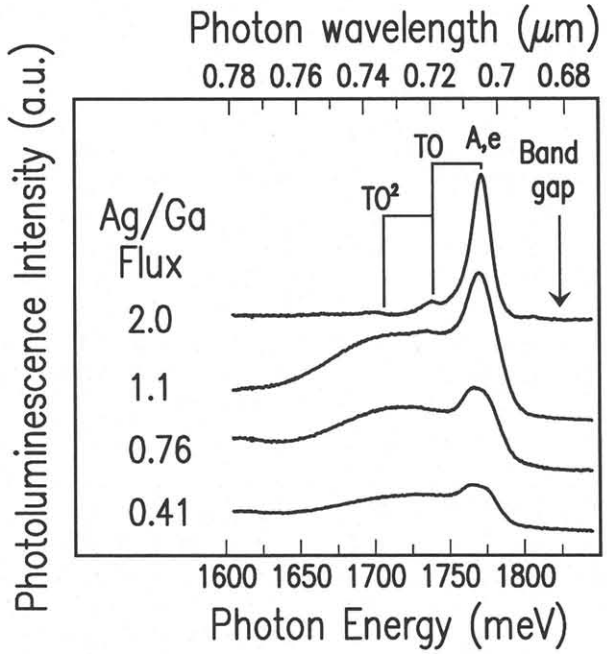

Fig 3. The photoluminescence spectra for the samples grown on GaAs. A clear free-to-bound (A,e) transition is seen in the top curve along with phonon assisted transitions (TO). The broad band in the lower traces may signal the presence of Ga_2Se_3.

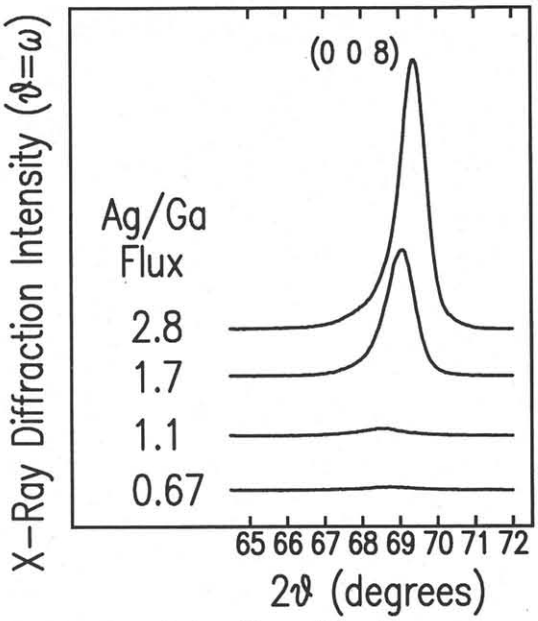

Fig 4. Growth on InAs. X-ray diffraction spectra near angles corresponding to the c-axis (008) reflection of $AgGaSe_2$. Curves for samples grown at four different silver/gallium ratios are shown.

4. Conclusions

Epitaxial growth of chalcopyrite $AgGaSe_2$ was achieved on both GaAs and InAs, but normal optical axis growth (required for second harmonic generation application) was only possible on the latter. Samples from near stoichiometry showed PL spectra comparable to the best reported results on bulk crystals.

Among several other tasks ahead remains the measurement of the non-linear optical parameters of the successfully grown epitaxial films.

Acknowledgments

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