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Structural and Optical Properties of Ga_2Se_3 Layers on GaAs(100)

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Abstract

High quality Ga_2Se_3 epitaxial layers were grown on GaAs(100) by a vapour phase growth method. The samples were studied by high resolution transmission electron microscopy (HRTEM), infrared specroscopy (IR), spectroscopic ellipsometry (SE), reflection and photoluminescence (PL) measurements. The layers formed consist of two parts which are separated by a sharp interface. The bottom part close to the substrate contains a considerable amount of voids while the well ordered β-phase dominates the upper part. The results obtained complement consistently the picture of the Ga_2Se_3 layers in terms of lattice dynamics and electronic bandstructure. Particularly a blue luminescence observed substantiates the potential for optoelectronic device applications.

Epitaxial Ga_2Se_3 layers have recently been discussed as potential candidates
optoelectronic devices[1, 2]. In order to improve the basic understanding of these
terial a combination of techniques providing information on structural and electr
properties was applied in this study.

The Ga_2Se_3 layers were prepared by a heterovalent exchange growth method
GaAs(100)[3]. The samples used in this study were grown at optimised growth p
meters [1] namely T_{GaAs}=860K and T_{Se}=560K, for 2 or 4 hours. HRTEM was
formed at 300kV by a Phillips EM430T fitted with energy dispersive X-ray anal
(EDX). Specimens for HRTEM were prepared in both ⟨100⟩ and ⟨110⟩ sections.
IR reflectance of the samples was measured at room temperature using Fourier
grating spectrometers and a gold mirror as reference. The SE spectra were recor
at room temperature using a rotating analyzer system with a Xe high pressure l
source. Reflection and photoluminescence measurements were carried out at 1.6K

From TEM images it is apparent that there are two main parts in the Ga_2Se_3
separated by a clear interface. The bottom layer is quite porous in nature w
the upper layer is fully dense. The lower layer is formed by replacing the ars

in GaAs by selenium. In this case Kirkendall type voids are expected to be present when differences in the diffusions rates between counter diffusing species arise. This certainly explains the porosity. Clearly no such problems arise in the case of the upper layer as new material is formed at the interface with the gas phase. This growth model is confirmed by a TEM image of a Ga_2Se_3 formed on a GaAs substrate partially masked with SiO_2. There the interface between the two Ga_2Se_3 layers coincides with the original GaAs surface. The interfacial region between the two adjacent layers is found to be arsenic rich as judged from EDX. Diffraction patterns taken along ⟨100⟩ differ quite markedly: the lower layer displaying only the sphalerite subcell reflections while the upper layer clearly shows the addional spots expected from the monoclinic unit cell of the ordered β-Ga_2Se_3 phase [4]. This diffraction pattern also shows that the Ga_2Se_3 cell is set in two directions related by a rotation of 90° in agreement with previous results [5]. When viewed along ⟨110⟩, high resolution imaging also revealed regions of another type of superstructure, namely a CuPt-type ordering. The same was observed in molecular beam epitaxy grown Ga_2Se_3 on GaP(100) [6]. However, the quality of the layers used in this study is superior to previous samples since HRTEM images reveal much better ordering throughout the entire upper layer. A more detailed discussion of the HRTEM results can be found in ref [7].

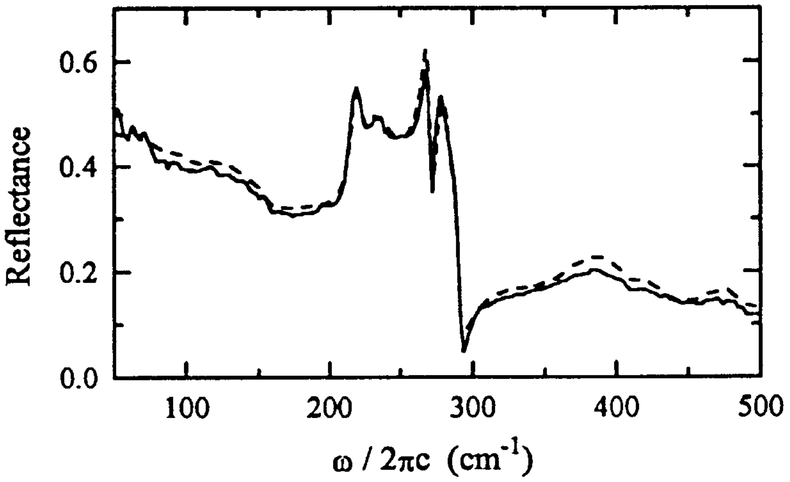

Figure 1: The far infrared reflectance of a 4h grown Ga_2Se_3 /GaAs sample (solid line). The dashed line corresponds to the best fit to the experimental data.

The IR reflectance in figure 1 reveals phonon features of both the Ga_2Se_3 layers as well as the GaAs substrate. A matrix formalism which uses the thicknesses and dielectric properties of each layer as input was applied to calculate the reflectance of the entire stack of layers [8]. The dielectric function of GaAs was derived from reflectance and transmittance measurements of a bare substrate. Using oscillator ansatzes the phonon contribution to the dielectric function of the Ga_2Se_3 layers was obtained from the best fit to the experimental data. Further measurements in the near IR (1000–10000cm^{-1}) yield the valence electron contribution ϵ_{VE} as well as the individual layer thicknesses. The parameters describing the system are summarized in table 1.

The longitudinal frequencies in the last column of table 1 were evaluated using the Lyddane-Sachs-Teller relation. The transverse and longitudinal frequencies (Ω_0 and ω_{LO}) compare very well with some peaks in the corresponding Raman spectra [1, 9] and allow the assignment of the Raman peaks at 220, 234, 273$cm^{-1}$and at 227, 241, 283$cm^{-1}$to transverse and longitudinal character, respectively. In addition the thicknesses from the IR fit confirm the HRTEM growth model.

Table 1: System parameters from IR data

layer	d [μm]	ϵ_{VE}	Ω_0[cm^{-1}]	Ω_P[cm^{-1}]	Ω_τ[cm^{-1}]	ω_{LO}[cm^{-1}]
top Ga$_2$Se$_3$	0.688	5.79	218.4	167.3	8.9	229
			231.2	180.2	15.7	243
			274.5	175.8	9.6	284
			285.8	73.20	8.0	287
bottom Ga$_2$Se$_3$	0.710	2.94	218.4	167.9	8.9	
			231.2	180.0	18.1	
			274.5	175.0	12.1	
			285.8	72.30	16.0	

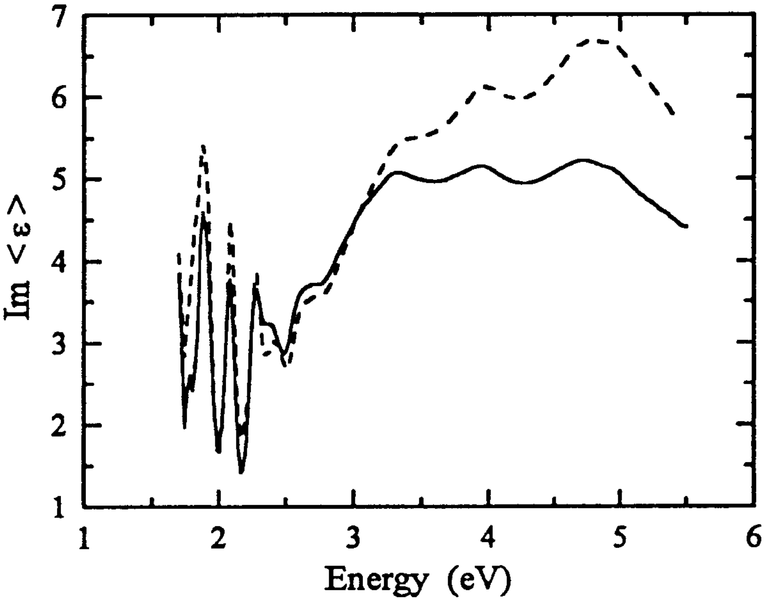

Figure 2: Imaginary part of the effective dielectric function of a 4h grown Ga$_2$Se$_3$ /GaAs sample.

SE yields the effective dielectric function of the Ga$_2$Se /GaAs samples from 1.8 t 5.5 eV [10]. The imaginary par for a typical sample is plotte in figure 2. The plane of incidence of light was parallel to th (011) and (01$\bar{1}$) plane of the sample for solid and dashed lines, respectively. The oscillations below 2.5eV are assigned to interference within the Ga$_2$Se$_3$ layer Beyond 2.5eV features are apparent which are most likely t be induced by interband critica points of the band structure. Th energy positions are 2.8, 3.3, 3.9 4.7, and 5.0eV. While there is excellent agreement with optical transition energies obtained from reflection spectra a 3.88 and 4.69eV [11], another transition energy was found to lie at 3.08 eV which i in between the first two features observed in this study. There is no evidence fo an energy gap near 2eV , which has also been reported previously [12]. However, th presence of minor absorbing features below 2.7eV cannot entirely be ruled out. Whil the overall lineshape is very simular for both sample orientations the magnitude varie significantly up to 35% . This optical anisotropy, which is also confirmed by reflectance anisotropy measurements, is induced by the ordered arrangement of vacancie forming columns along the ⟨01$\bar{1}$⟩ direction [2].

Two excitonic features can be seen in the reflection spectrum of figure 3 betwee 3.11 and 3.15eV. The strong variation of the reflectivity is indicative for a direct ban gap consistent with the SE results.

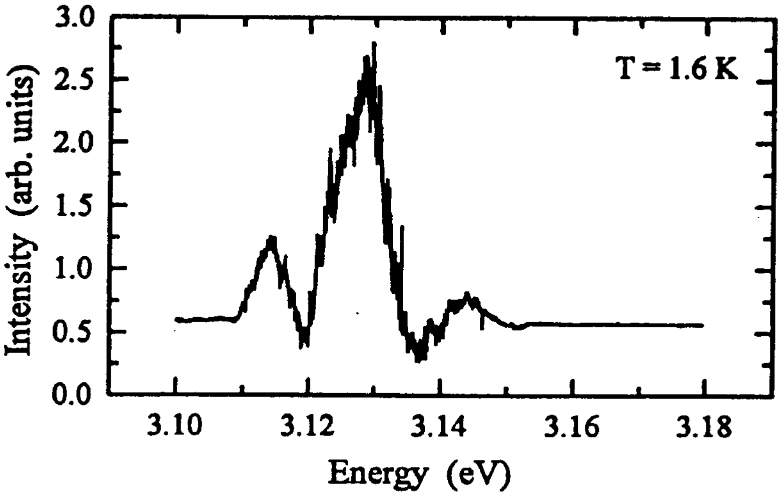

Figure 3: Reflection of a 4h grown Ga_2Se_3 /GaAs sample.

The occurence of two reflection loops is likely to be explained by a valence band splitting as a result of strain in the Ga_2Se_3 layer. Further confirmation for an energy gap in the blue spectral range is found in the PL spectra excited by UV light (3.76eV). They exist of a single strong broad band peaked at 3.10eV.

The findings of this study are further support for our previous suggestion that high quality epitaxial Ga_2Se_3 layers are potential competitors in the II-VI dominated wide gap domain.

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References

1. D.R.T.Zahn, A.Krost, M.Kolodziejczyk, and W.Richter, *J. Vac.Sci.Technol.* **B10** (1992) 2077.
2. T.Okamoto, N.Kojima, A.Yamada, M.Konagai, K.Takahashi, Y.Nakamura, and O.Nittono, *Jpn.J.Appl.Phys.* **31** (1992) L143.
3. M.Kolodziejczyk, Th.Filz, A.Krost, W.Richter, and D.R.T.Zahn, *J.Crystal Growth* **117** (1992) 549.
4. D.Lübbers and V.Leute, *J.Solid State Chem.* **43** (1982) 339.
5. A.C.Wright, J.O.Williams, A.Krost, W.Richter, and D.R.T.Zahn, *J.Crystal Growth* **121** (1992) 111.
6. N.Teraguchi, F.Kato, M.Konagai, K.Takahashi, Y.Nakamura, and N.Otsuka, *Appl.Phys.Lett.* **59** (1991) 567.
7. A.C.Wright, J.O.Williams, M.von der Emde, D.R.T.Zahn, A.Krost, and W.Richter, in *Proceedings of MSM-8, 5.-8.April 1993, Oxford, UK.*
8. S.Morley, D.R.T.Zahn, T.Eickhoff, W.Richter, D.A.Woolf, D.I.Westwood, and R.H.Williams, *J.Appl.Phys.* **72** (1992) 631.
9. E.Finkman, J.Tauc, R.Kershaw, and A.Wold, *Phys. Rev. B* **11** (1974) 3785.
10. D.E.Aspnes, A.H.Studna, *Appl. Opt.* **14** (1975) 220.
11. A.E.Bakhyshev, L.G.Musaeva, and G.A.Akhundov, *phys.stat. sol.* **B54** (1972) K77.
12. Landolt-Börnstein, *New Series Vol.III/17a* (Springer Verlag, Berlin, Heidelberg, New York, 1982).