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Deposition and characterization of Ga_2Se_3 thin films prepared by a novel chemical close-spaced vapour transport technique

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Abstract

Single-phase Ga_2Se_3 films have been deposited with a growth rate of about 30 nm min^{-1} on clean and Mo-coated soda-lime glass substrates by chemical close-spaced vapour transport. The use of HCl/H_2 as a transport agent results in a stoichiometric volatilization of the binary Ga_2Se_3 powder source material and the growth of Ga_2Se_3 films with reproducible composition. The films have been characterized using x-ray diffraction measurements, scanning electron microscopy observations, energy dispersive x-ray analysis, x-ray fluorescence spectrometry and elastic recoil detection analysis. A p-type conductivity was determined by means of the thermoelectric probe method. A Ga_2Se_3 band gap energy $E_g = 2.56$ eV has been found by optical measurements.

1. Introduction

The III–VI semiconductor compounds, such as Ga_2Se_3, have in the past received attention because of their structural properties—Ga_2Se_3 is a defect semiconductor which crystallizes in a zincblende-like structure in which one third of the cationic sites is vacant [1]. Ga_2Se_3 crystallizes, mainly, in α and β structural modifications. In the α-form, the vacancies are randomly distributed at the cationic sites, while the β-form shows zigzag-ordered vacancies, arranged in a superstructure originating from the α-Ga_2Se_3 structure [2, 3]. Recently, interest in the III–VI defect compounds—especially Ga sesqui-chalcogenides—has increased as they are promising materials for use in optoelectronic devices [4] and are good candidates for the passivation of heterogeneous ZnSe/GaAs interfaces [5].

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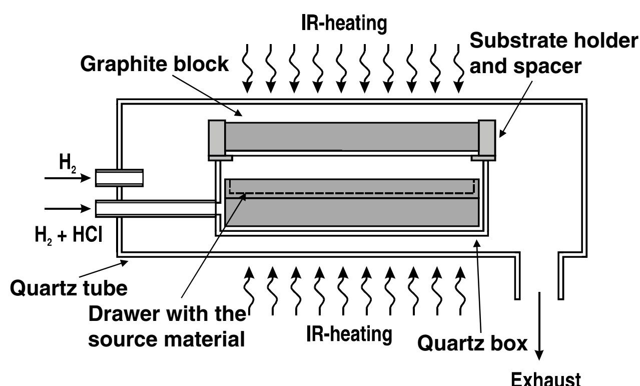


Figure 1. Schematic drawing of the CCSVT apparatus.

The III–VI semiconductors are also used for the preparation of I–III–VI chalcopyrite semiconductors as absorber materials for solar cells [6–8]. Usually, absorber thin films in high efficiency solar cells based on I–III–VI compounds are prepared by physical vapour deposition methods such as co-evaporation of the elements [9, 10] and molecular beam deposition [11] which require high temperatures for the employed evaporation sources. However, the energy consumption of the preparation process of I–III–VI thin films can be significantly decreased by using III–VI compounds, such as In_2Se_3 and Ga_2Se_3, exhibiting low sublimation temperatures, in combination with copper-selenides and -sulphides. Moreover, chemical vapour transport (CVT) techniques can be applied for a faster volatilization of binary source materials, by reactions with halogens such as molecular I_2, Cl_2 or HCl, to gaseous halogenides at moderate temperatures [7]. On the other hand, the CVT process requires a long-term stability of the binary source material for the deposition of III–VI compounds at controlled growth conditions.

In this paper, we report on the film growth of Ga_2Se_3 on uncoated and Mo-coated glass substrates by means of the novel chemical close-spaced vapour transport (CCSVT) deposition technique using gaseous HCl/H_2 as a volatilization and transport agent. Structural and optical properties of the Ga_2Se_3 thin films will be also given since the properties of the material are not yet well established.

2. Experimental details

2.1. Growth of Ga_2Se_3 thin films

For the deposition of Ga_2Se_3 thin films, a novel CCSVT apparatus (AIXTRON AG) has been developed. A schematic drawing of the system is shown in figure 1. The CCSVT graphite-made reaction cell is placed in a quartz box which has an inlet tube for the gaseous HCl, used for volatilization of the Ga_2Se_3 source material. A spacer is used for adjusting the distance between the source drawer and substrate holder, where 9 substrates (area 1 inch^2) can be mounted. The source material in the form of fine grained powder fills the source drawer, which allows easy refilling. The quartz box with the CCSVT cell is placed in a quartz tube which can be evacuated or filled with H_2. The reactor pressure can be varied from 10^{-2} mbar up to 1000 mbar. Collectively arranged infrared units (12 infrared lamps—1000 W each) are used as heaters for the source drawer and the substrate. The temperatures are controlled by thermocouples at the source and substrate side and can be set independently.

The Ga_2Se_3 source material has been synthesized from the 6N-pure elements. Gaseous HCl diluted in H_2 is used as transport agent, while additional hydrogen serves as ambience in the quartz tube which surrounds the reaction cell. Clean and Mo-coated (Mo thickness of $\approx 1\ \mu$m) soda-lime glass (SLG) substrates were used for the Ga_2Se_3 deposition. The Ga_2Se_3 thin-film deposition was performed under varying conditions of the source temperature (T_{source}), the substrate temperature ($T_{\mathrm{substrate}}$), the distance between source material and substrate holder ($D_{\mathrm{source-substrate}}$), the reactor pressure (p_{reactor}), and the gaseous HCl content within the H_2 carrier gas ($Q_{\mathrm{HCl}}/Q_{\mathrm{H_2}}$): $p_{\mathrm{reactor}} = 300$–$800$ mbar, $D_{\mathrm{source-substrate}} = 8$–$18$ mm, $Q_{\mathrm{HCl}}/Q_{\mathrm{H_2}} = 10/1$, $T_{\mathrm{source}} = 520$–$580\,^{\circ}$C, $T_{\mathrm{substrate}} = 420$–$480\,^{\circ}$C. The temperature difference between source and substrate was kept at $100\,^{\circ}$C.

2.2. Characterization techniques

The deposited films were characterized by means of x-ray diffraction (XRD) with a Bruker D8 diffractometer with Cu Kα excitation ($\lambda = 1.5418$ Å) in order to identify crystallographic phases. The surface morphology of the films was studied by scanning electron microscopy (SEM) by using a Leica/Zeiss LEO430 system. The film stoichiometry was investigated by energy dispersive x-ray analysis (EDX, Röntec M2 detector) and x-ray fluorescence spectrometry (XRF) with a Philips MagiXPRO PW 2400 spectrometer. An elastic recoil detection analysis (ERDA) technique using 230 MeV ^{129}Xe ions as projectiles was applied at the Ionenstrahllabor (ISL) of the Hahn-Meitner-Institut to obtain the absolute atomic concentrations as a function of film depth. Details of the ERDA principle and the experimental setup can be found in [12]. Optical reflection and transmittance measurements were performed at 300 K using a Cary 500 spectrometer (Varian) in combination with an integrating sphere in order to collect the scattered light. The Ga_2Se_3-type conductivity was determined by the thermoelectric probe method.

3. Results and discussion

3.1. Ga_2Se_3 source stability

The verification of phase stability and, hence, the checking of stoichiometric alterations of the binary Ga_2Se_3 source material as well as the reproducibility of the source material volatilization was an important task at the beginning of the deposition studies. Thus, the binary Ga_2Se_3 source material was investigated by means of EDX and XRD (not shown) before and after the process performance at $T_{\mathrm{source}} = 520$–$580\,^{\circ}$C and a total deposition duration of 11.5 and 38.5 h, respectively (see table 1). EDX measurements revealed a slightly Ga-rich composition which remained constant during the process performance (± 3 at.%), while XRD data showed no structural or compositional phase change within the resolution limit of the measurements.

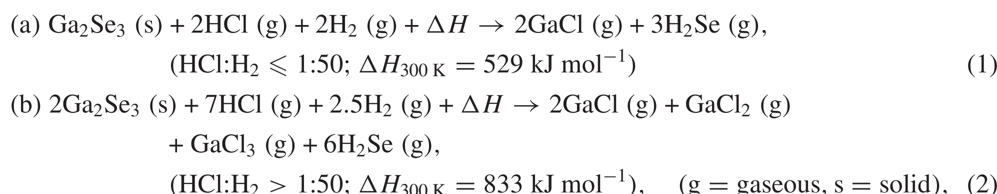
3.2. Physical properties of Ga_2Se_3 thin films

Due to the phase stability of the observed source material, we assume that the volatilized gas phase compounds of Ga_2Se_3, GaCl and H_2Se (see equations (1), (2)), also remain constant in composition and concentration. At an HCl to H_2 concentration ratio of $\mathrm{HCl{:}H_2} \leqslant 1{:}50$ (equation (1)) mainly gallium monochloride was observed, while at a very high HCl to hydrogen concentration ratio $\mathrm{HCl{:}H_2} > 1{:}50$ gallium di- and trichloride was also formed (see equation (2)). On the other hand, the reaction of hydrogen with Ga_2Se_3 towards forming metallic Ga and gaseous H_2Se can only be observed at very low HCl concentrations. In the

Table 1. Compositional and phase stability of the Ga_2Se_3 source before and after the process performance ($T_{source} = 520–580\,°C$, $p_{reactor} = 300–800$ mbar and a total deposition time of 11.5 and 38.5 h) as measured by energy dispersive x-ray (EDX) analysis and x-ray diffraction (XRD).

Source material	Exposure time to HCl (h)	EDX (at.%)		XRD
		Ga	Se	
Ga_2Se_3	0	41.9	58.1	Single-phase (JCPDS 44-1012)
Ga_2Se_3	11.5	41.3	58.7	Single-phase (JCPDS 44-1012)
Ga_2Se_3	38.5	41.7	58.3	Single-phase (JCPDS 44-1012)

equilibrium state, the reaction of gaseous HCl and H_2 with solid (state) Ga_2Se_3 can be expressed by



$$\text{(a) } Ga_2Se_3\ (s) + 2HCl\ (g) + 2H_2\ (g) + \Delta H \rightarrow 2GaCl\ (g) + 3H_2Se\ (g), \quad (HCl{:}H_2 \leqslant 1{:}50;\ \Delta H_{300\,K} = 529\ \text{kJ mol}^{-1}) \tag{1}$$

$$\text{(b) } 2Ga_2Se_3\ (s) + 7HCl\ (g) + 2.5H_2\ (g) + \Delta H \rightarrow 2GaCl\ (g) + GaCl_2\ (g) + GaCl_3\ (g) + 6H_2Se\ (g), \quad (HCl{:}H_2 > 1{:}50;\ \Delta H_{300\,K} = 833\ \text{kJ mol}^{-1}), \quad (g = \text{gaseous}, s = \text{solid}), \tag{2}$$

where ΔH is the reaction's enthalpy.

These stable and reproducible reaction conditions resulted in the deposition of single-phase Ga_2Se_3 films under all applied process conditions. Figure 2 shows the XRD pattern of the Ga_2Se_3 thin films grown on Mo/glass substrates at $T_{source} = 520–580\,°C$, $T_{substrate} = 420–480\,°C$ and $Q_{HCl}/Q_{H_2} = 10/1$, $D_{source-substrate} = 8$ mm, $p_{reactor} = 800$ mbar and a deposition time of 30 min. All patterns exhibit the same peak positions according to JCPDS 44-1012 [13], indicating the same phase of the grown Ga_2Se_3. The diffractogram for $T_{substrate} = 450\,°C$ (see figure 2(b)) shows most clearly the (131) and (004) peaks, so this temperature yields the best crystallinity for the films. The peak positions and their relative intensities according to JCPDS 44-1012 data are presented in figure 2 as lines, corresponding to the monoclinic structure of the β-Ga_2Se_3. By comparison of the XRD diffractograms of the films prepared by CCSVT in the present study with the data of [13], we assume a β modification for the deposited Ga_2Se_3 which correlates well with the SEM observations.

The surface morphology of the films (see figures 3(a), (b)) depends on the applied temperatures $T_{source/substrate}$, implying changes in the crystallite shapes. At a reactor pressure of 800 mbar and $T_{substrate} = 450\,°C$, continuous layers with grain sizes of up to 500 nm showing parallelepiped-like shapes were found (figure 3(b)), while at $T_{substrate} = 420\,°C$ triangular-like grain shapes were observed (figure 3(a)). At a higher deposition temperature of $T_{substrate} = 480\,°C$ the layers exhibit some pinholes (not shown). Both, triangular and parallelepiped-like grains of the layers presented in the SEM pictures of figure 3 can be attributed to an orthorhombic and a monoclinic structure, respectively, of the β-Ga_2Se_3 as long as the monoclinic structure is considered to be a superstructure originating from the orthorhombic one [14], and no significant differences in the structural and electronic properties are found between the two ordered structures [14]. Triangular ridges in the vacancy-ordered films were also observed by Okamoto *et al* [15].

The EDX and XRF chemical analyses of the films reveal a stoichiometric composition of deposited films at the applied deposition conditions at a reactor pressure of 600 mbar or higher. On the other hand, for reactor pressures below 600 mbar, stoichiometric films are found only for a distance between source and substrate of $D_{source-substrate} = 8$ mm. The investigated

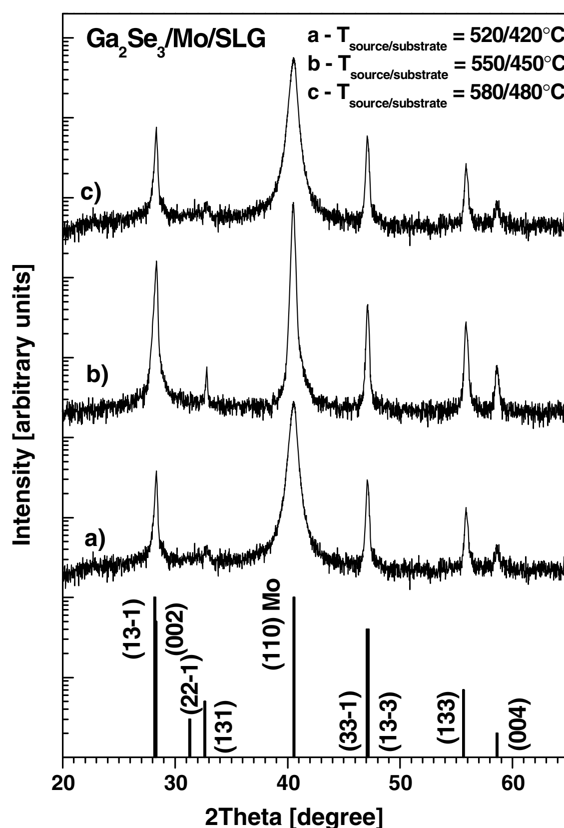


Figure 2. XRD diffractograms of the Ga_2Se_3 thin films grown on Mo/glass substrates at different source and substrate temperatures and $Q_{HCl}/Q_{H_2} = 10/1$, $D_{source-substrate} = 8$ mm, $p_{reactor} = 800$ mbar and deposition time of 30 min. The lines mark the Ga_2Se_3 and Mo peak positions and their relative intensities according to JCPDS 44-1012 and JCPDS 42-1120, respectively.

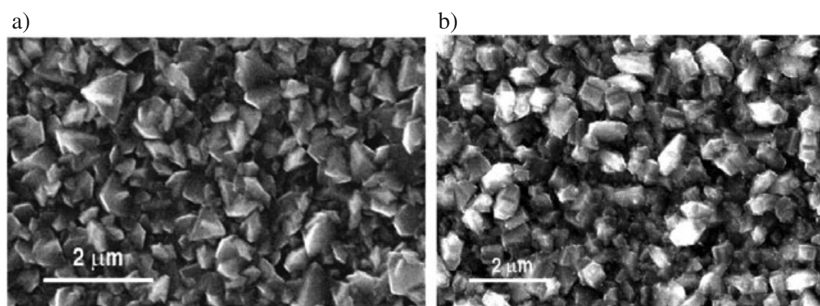


Figure 3. Top view SEM images of the Ga_2Se_3 thin films grown on Mo/glass substrates at $Q_{HCl}/Q_{H_2} = 10/1$, $D_{source-substrate} = 8$ mm, $p_{reactor} = 800$ mbar and (a) $T_{source} = 520\,°C$, $T_{substrate} = 420\,°C$, at a deposition rate of 20 nm min^{-1}, and (b) $T_{source} = 550\,°C$, $T_{substrate} = 450\,°C$, at a deposition rate of 23 nm min^{-1}.

films show only a small amount (~0.5 at.%) of Cl detected by XRF spectrometry. Typical compositional data are presented in table 2.

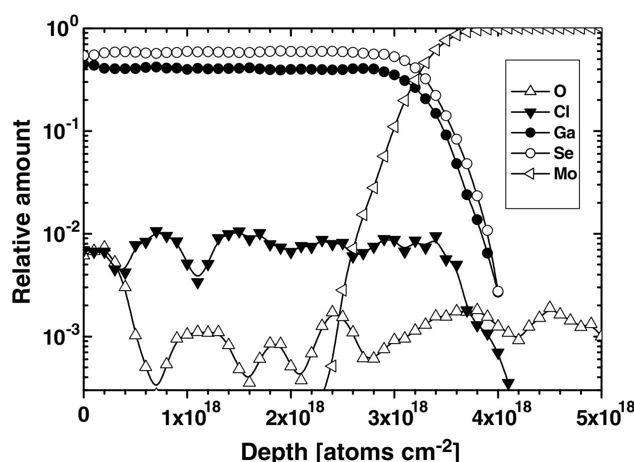


Figure 4. Relative amounts of the elements versus depth measured on Ga_2Se_3/Mo/glass structures by ERDA.

Table 2. The results of the Ga_2Se_3 thin-film characterization by XRD and EDX analyses, and XRF spectrometry.

		EDX (at.%)		XRF (at.%)		
Sample ID	XRD	Ga	Se	Ga	Se	Cl
1	Single-phase (JCPDS 44-1012)	40.8	59.2	39.54	59.95	0.51
2	Single-phase (JCPDS 44-1012)	41.0	59.0	39.77	59.70	0.53

By means of the ERDA technique, high depth homogeneity of the deposited layer was observed (figure 4). Ga_2Se_3/Mo/SLG structures were reconstructed from the measured energy spectra using the program Konzerd [16]. Insignificant amounts of H_2 (0.05 at.%), O_2 (0.07 at.%) and Al (0.06 at.%) were determined using the SimNRA simulation program [17]. Chlorine was found as a major contaminant and was detected within the deposited Ga_2Se_3 films at an almost constant level of 0.85 at.%. The thickness of the investigated Ga_2Se_3 thin films of 830 nm was calculated using the bulk density of Ga_2Se_3. Furthermore, a Ga_2O_3 surface layer (about 2×10^{15} atom cm^{-2}—calculated from an integral method using the SimNRA program) was found on the top side of the Ga_2Se_3 due to exposure to air. Because of the roughness, the possible surface layers are broadened in depth, as seen in figure 4 for the oxygen profile of the Ga_2O_3 layer. This, however, does not influence the profiles and concentration of the elements in the bulk.

It was found that the film-deposition rate and the deposited area depends strongly on the reactor pressure. The film-deposition rate increases almost linearly with the reactor pressure and a deposition rate of $\approx$30 nm min^{-1} is determined at optimum Ga_2Se_3 thin-film deposition conditions: $T_{\mathrm{source}} = 550\,^{\circ}\mathrm{C}$, $T_{\mathrm{substrate}} = 450\,^{\circ}\mathrm{C}$, $p_{\mathrm{reactor}} = 800$ mbar, $D_{\mathrm{source-substrate}} = 8$ mm, $Q_{\mathrm{HCl}}/Q_{\mathrm{H_2}} = 10/1$. The application of these deposition conditions results in a completely covered substrate area of 10×10 cm^2.

3.3. Optical properties

The absorption coefficient of a 418 nm thin film grown at optimum deposition conditions has been calculated using equation (3) [18] and by means of optical transmission and reflection

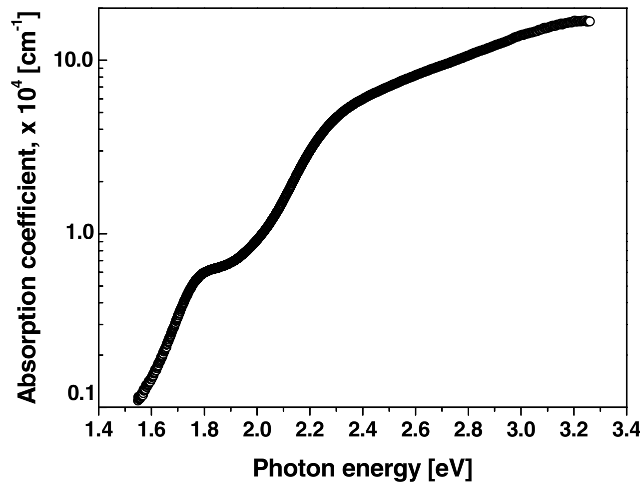


Figure 5. Absorption coefficient versus photon energy for a Ga_2Se_3 thin film grown at 450 °C.

data taken at 300 K:

$$\alpha = -\frac{1}{t}\ln\left(\frac{\sqrt{(1-R)^4 + 4T^2R^2} - (1-R)^2}{2TR^2}\right), \tag{3}$$

where α is the absorption coefficient, t is the thickness of the film, T and R are the transmission and reflectance, respectively. A detailed analysis of the absorption coefficient data revealed the presence of several optical transitions. Figure 5 shows the absorption coefficient as a function of the photon energy.

The main absorption appears in the high photon energy region, but, additional absorption features are found in the low energy range from 1.6 to 2.3 eV with much smaller values. This suggests that band-to-band optical transitions occur in the high photon energy region ($h\nu > 2.3$ eV), while, on the other hand, transitions between the valence band and an ionized donor or, alternatively, between an ionized acceptor and the conduction band appear in the lower energy region. In [14] and [19] it was reported that the β-Ga_2Se_3 phase also exhibits a direct forbidden energy gap. In the case of allowed direct transitions, the absorption coefficient has the following spectral dependence [20]:

$$\alpha(h\nu) = A(h\nu - E_g)^{1/2}, \tag{4}$$

where A is a constant and E_g is the corresponding semiconductor band gap. Thus, the optical band gap of the Ga_2Se_3 was determined to be about 2.56 eV by extrapolation of the linear part of the spectrum $\alpha^2 = f(h\nu)$ to zero (figure 6).

As mentioned, additional absorption processes occur in the range of $1.6\,\text{eV} < h\nu < 2.3\,\text{eV}$. By extrapolation, as described above but assuming in expression (4) $E_g - E_a$ instead of E_g, energy values of 1.66 and 2.14 eV were extracted from figures 6(a) and (b), respectively, where E_a is the activation energy of the corresponding level in the forbidden band gap. Thus, a trap level with an activation energy of about 900 meV and a deep level with an activation energy of 420 meV participate in the absorption process in Ga_2Se_3 at 300 K.

In the literature, the reported band gap energy values of Ga_2Se_3 vary from 2.1 eV [21] to 2.3 eV [19], 2.4 eV [14], and 2.7 eV [22]. However, it was found in this work by means of optical measurements that the β-Ga_2Se_3 phase exhibits a band gap energy of $\sim$2.56 eV, furthermore, the transition energies lying in between the energy gap value and 2.1 eV can

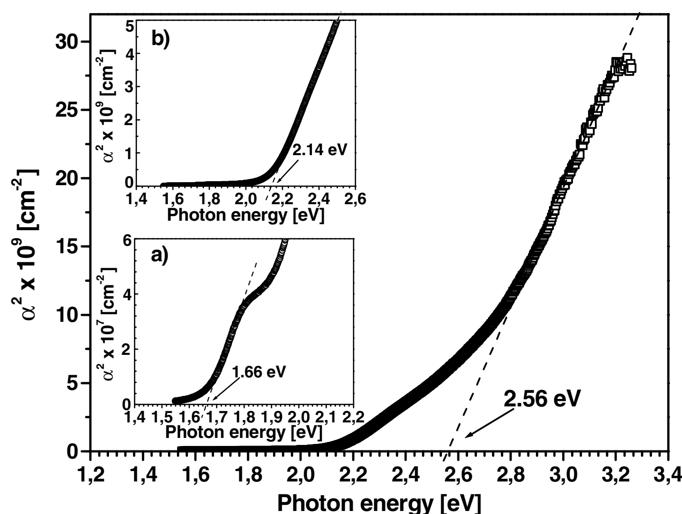


Figure 6. α^2 versus photon energy for a Ga_2Se_3 thin film grown at 450 °C. A Ga_2Se_3 band gap energy of $E_g = 2.56$ eV it is determined by extrapolation of the linear part of the spectrum $\alpha^2 = f(h\nu)$ to zero. The insets show an additional analysis of the optical absorption spectrum in the photon energy range from 1.6 to 2.3 eV for direct allowed transitions with (a) $E_g - E_a = 1.66$ eV and (b) $E_g - E_a = 2.14$ eV, where E_g is the band gap energy and E_a is the activation energy.

be attributed to a band-to-impurity level transition. Moreover, it is proposed that, due to the presence of an impurity band close to the conduction band minimum, additional transitions are observed and that this impurity band also narrows the Ga_2Se_3 forbidden band gap (see band gap energies reported in [14, 19, 21]). The width of the proposed impurity band depends, probably, on the growth conditions.

The p-type conductivity of as-grown Ga_2Se_3 thin films has been determined by the sign of the Seebeck voltage in the thermoelectric probe method.

4. Conclusion

Single-phase β-Ga_2Se_3 thin films have been deposited at a growth rate of about 30 nm min^{-1} on clean and Mo-coated SLG substrates in a novel CCSVT system (AIXTRON AG). The utilization of the gaseous HCl as transport agent diluted with hydrogen (with a ratio of $HCl:H_2 = 10:1$) results in a stable volatilization of the binary Ga_2Se_3 powder source material and a reproducible growth of stoichiometric Ga_2Se_3 thin films. An optimum set of deposition parameters for the growth process have been worked out, such as $T_{source} = 550$ °C, $T_{substrate} = 450$ °C, $p_{reactor} = 800$ mbar, $D_{source-substrate} = 8$ mm, $Q_{HCl}/Q_{H_2} = 10/1$.

A band gap energy of $E_g = 2.56$ eV has been determined by optical measurements for single-phase Ga_2Se_3 thin films. The p-type conductivity was determined by performing Seebeck measurements.

In summary, a highly stable and reproducible process for application in photovoltaic thin-film deposition has been successfully installed, tested and demonstrated by using binary Ga_2Se_3 semiconducting material. Thus, the novel CCSVT method can be regarded as a very promising deposition technique for the large-scale application of III–VI semiconductors and also for application to ternary I–III–VI chalcopyrite semiconductors (research on which is currently in progress [23]).

Acknowledgments

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