Chapter 6
Electron spin resonance of as-grown and Ge- implanted $CuGaSe_2$ thin films

Continuous wave (cw) electron spin resonance (ESR) is powerful method to investigate paramagnetic defect states in materials because it is a sensitive indicator of the local environment of defects. In this chapter ESR measurements are used to investigate whether Ge incorporation into $CuGaSe_2$ thin films can induce paramagnetic centers. Therefore, ESR spectra of Ge- implanted films in comparison to the as- grown films were analyzed and also the concentration of paramagnetic centers in the doped films was determined. In section 6.1, an experimental description of the ESR measurements is given, followed in section 6.2 by the results of the ESR on the Ge doped and as-grown $CuGaSe_2$ films. Section 6.3 deals with the Curie paramagnetism in the Ge implanted films and in section 6.3, the microscopic origin of Curie paramagnetism in the Ge implanted films is analyzed.

6.1 Experimental details

The Ge content and depth profile of both annealed and as-implanted polycrystalline $CuGaSe_2$ samples were determined by Secondary Neutral Mass Spectroscopy (SNMS) (see chapter 5). ESR was used to evaluate the concentration of paramagnetic centers using a Bruker Elexsys 580 spectrometer operating at X-band microwave frequencies (9.5 GHz) in the temperature range 5 – 300 K. For ESR measurements, the implanted $CuGaSe_2$ films were peeled off from the glass substrate with adhesive ESR silent Tesa-tape because of the characteristic bent structure of $MoSe_2$ interfacial layer which forms during the growth between the Mo layer and the $CuGaSe_2$ film [85, 86, 87]. Afterward, the peeled off $CuGaSe_2$ films were then rolled up and placed in sealed quartz tubes previously filled with He. The amount of spins was determined by comparison with a spin calibrated standard sample, namely, a sputtered a-Si sample.

6.2 Paramagnetic centers in as- grown and Ge- implanted $CuGaSe_2$ thin films.

6.2.1 Paramagnetic activity of Ge in $CuGaSe_2$.

After Ge implantation and annealing and assuming that all the Ge atoms do not occupy the interstitial lattice sites, the possible Ge occupation on Cu or Ga or Se sites gives rise to different electron configurations as summarized in the table 6.1

Table 6.1: *Possible Ge occupation of the $CuGaSe_2$ sites and the resulting electron configuration and paramagnetism activity.*

Ge occupation	Electron configuration	Paramagnetism activity
Ge_{Cu}^{3+}	[Ar]$4s^1$	Yes
Ge_{Ga}^{1+}	[Ar]$4s^2 4p^1$	Yes
Ge_{Se}^{2-}	[Ar]$4s^2 4p^4$	No

From table 6.1, electron spin resonance signals are to be expected when Ge occupies Cu or Ga sites because of the resulting unpaired electron, while no ESR signal may occur when Ge occupies Se sites.

6.2.2 ESR of as grown and Ge implanted $CuGaSe_2$ films.

Figure 6.1 shows the ESR spectrum of as- grown; as- grown and annealed; Ge- implanted and annealed $CuGaSe_2$ films.

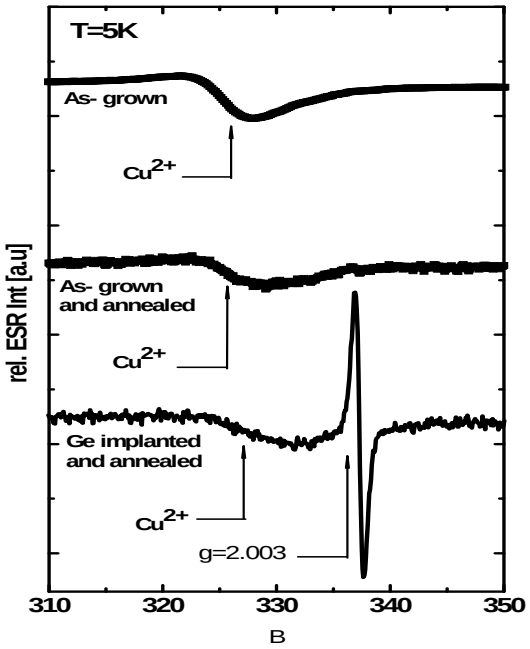


Figure 6.1: *ESR spectra of as-grown; as-grown and annealed; Ge implanted and annealed* $CuGaSe_2$ *thin films all taken at T=5K. It is clearly noticeable that a new ESR signal*

appears at g = 2.003 for Ge implanted samples.

The spectrum of as- grown films exhibits an asymmetric and broad ESR resonance at 323 ± 0.5 mT. For the Ge implanted and annealed samples, in addition to the Cu^{2+} signal, an intense, narrow, Lorentzian shaped signal with the Landé g-factor, $g = 2.003$, and peak-to peak width $\Delta Hpp \sim 7$G is observed, as depicted in figure 6.2.

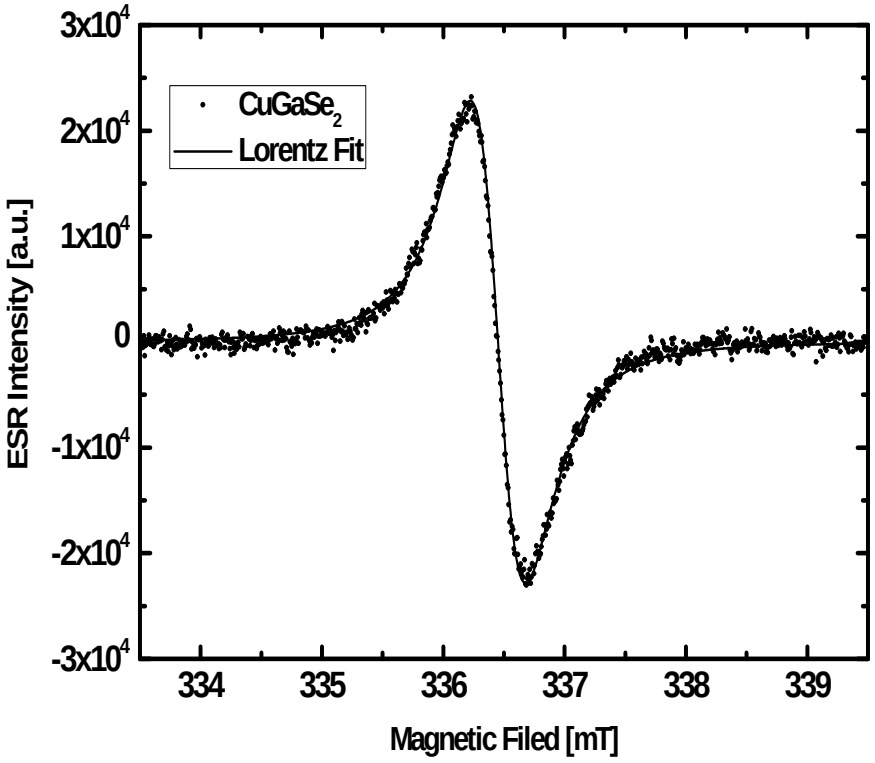


Figure 6.2: *ESR signal at g = 2.003 measured at T = 5K. The solid line is the result of fitting with the first derivative of Lorentzian function.*

6.2.3 Assignment of ESR signals.

The broad and isotropic ESR signal found in as-grown $CuGaSe_2$ films was also observed after ageing and oxidation of the films [88, 89, 90]. Based on previous work carried out in detail by R. Würz [88], the origin of this signal was ascertained and therefore assigned to Cu^{+2} stemming from the formation of a $Cu^{2+}(OH)_2^-$ surface hydroxide phase after long term ageing. The ESR resonance at $g = 2.003$, with a g value close to that of a free electron at $g = 2.0023$, is observed exclusively in Ge containing films. The ESR signal at $g = 2.003$ resembles resonances that have been previously reported for ZnSe and I-III-VI_2 chalcopyrite compounds in a g- value range of 2.003 – 2.006 and is summarized in table 6.2

Table 6.2: *Narrow ESR signal ranging from 2.002 - 2.006, observed for chalcopyrite compounds and ZnSe.*

Compound	g factor	Assignment	Reference
ZnSe	2.0027	V_{Se}^{+}	[91]
$CuGaSe_2$	2.006	V_{Se}^{+}	[92]
$CuInSe_2$	2.003	In_{Cu}	[93]
$CuInS_2$	2.0012	V_S	[94]
Cu(In, Ga)Se_2	2.002	In_{Cu}	[95]
	2.0012-2.005	In_{Cu}	[96]

Table 6.2 lists all the observed narrow ESR signals around $g = 2.00$ for chalcopyrite compounds and ZnSe. In the ESR spectra of electron-irradiated $CuIn_xGa_{1-x}Se_2$, Okada and collaborators [97] assigned the line at $g = 2.003$ to electrons trapped by donor states induced by In_{Cu} point defects. Previously, Sato et al [95] proposed a model in which they ascribed this ESR signal to singly ionized donors (V_{Se}^{+} and In_{Cu}^{+}). Nishi et al [92, 98] observed a comparable signal in as-grown $CuGaSe_2$ compounds and $CuGaSe_2$ annealed under H_2 and O_2 atmosphere and attributed this ESR resonance to positively- charged Se vacancies (V_{Se}^{+}). In all the above mentioned investigations, the microscopic origin of ESR signals with g- factors in the range of 2.003 and 2.006 was not fully understood. The only agreement met by all these observations is that the ESR lines originate from electrons localized at donor states.

6.3 Curie paramagnetism of Ge implanted $CuGaSe_2$ films

In order to gain more information about the origin of the ESR resonance at $g = 2.003$, the ESR spectra of all the Ge implanted films were measured as a function of temperature. From the temperature dependence of ESR spectra, it is possible to predict whether a resonance is due to Curie- type localized states or to delocalized states, which in turn are due to Pauli paramagnetism. The static susceptibility χ_0 of an ESR signal is proportional to the magnetization M_0

$$M_0 = \frac{1}{2} g \mu_B \Delta N = \frac{1}{\mu_0} \chi_0 B_0 \tag{6.1}$$

Where μ_0 denotes the vacuum permeability, μ_B the Bohr magneton. ΔN, the total number of spins is given by:

$$\Delta N = N_{spin\ up} - N_{spin\ down}$$

here $N_{spin\ up}$, $N_{spin\ down}$ are the populations of spin of the upper and lower levels, respectively. In the case of Curie paramagnetism, the static susceptibility χ_0 is related to the g- factor, the number of spins of the sample ΔN^{Curie} and the temperature of the sample T, by the Curie law:

$$\chi_0 = \frac{\Delta N^{Curie} g^2 \mu_0 \mu_B^2}{4 k_B T} \tag{6.2}$$

where k_B is the Boltzmann constant. Figure 6.3 represents the normalized temperature dependence of the paramagnetic susceptibility χ_0 for all the three Ge implanted films at the $g = 2.003$ resonance.

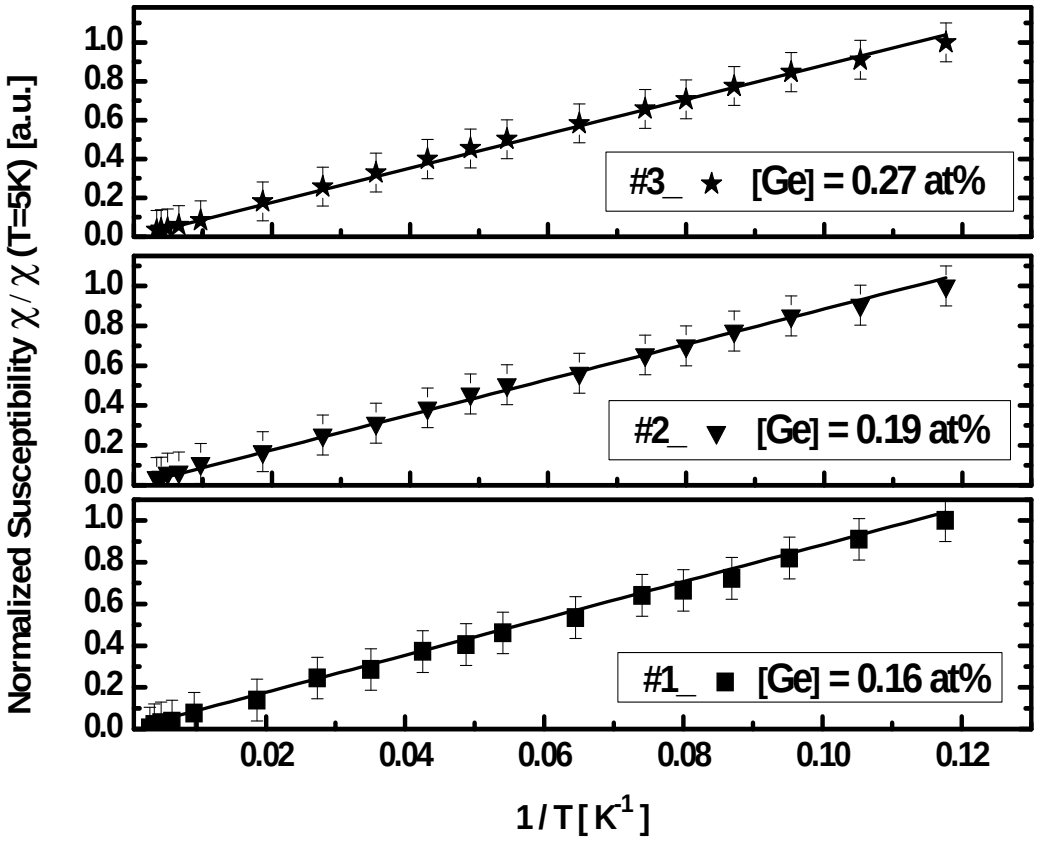


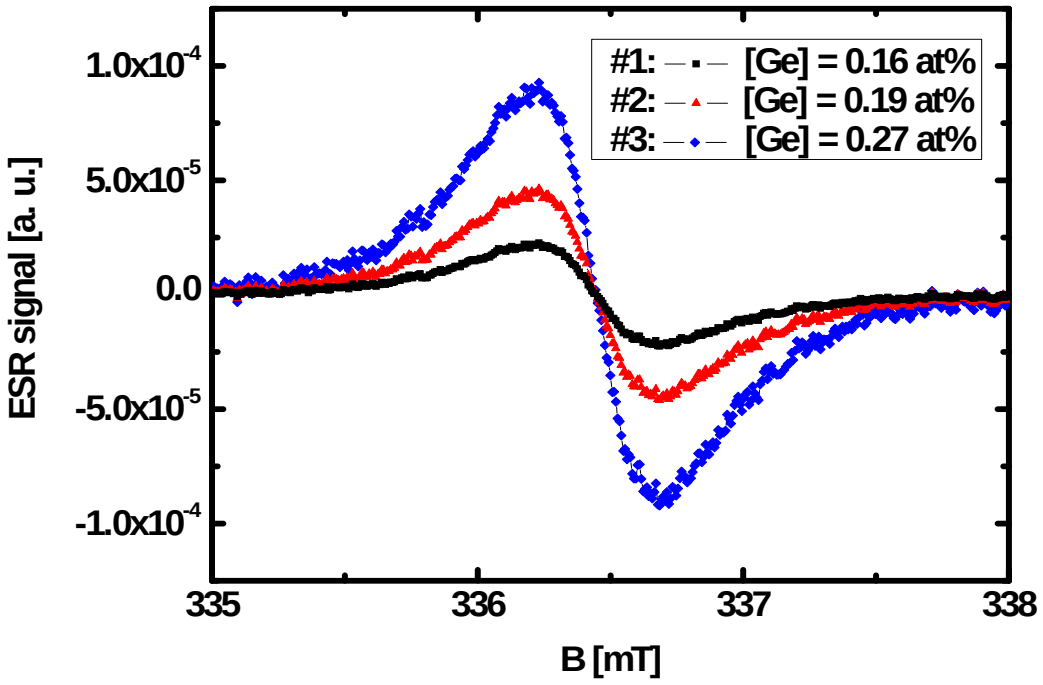
Figure 6.3: *Temperature dependence of the normalized paramagnetic susceptibility χ_0 of Ge implanted $CuGaSe_2$ films for different Ge concentrations. The solid line is fit assuming Curie- type susceptibility.*

The susceptibility of this ESR signal follows a Curie law in the temperature range 5 – 300 K, without any trace of Pauli paramagnetism. Such a Curie-temperature dependence is only expected for paramagnetic sites that are localized in the band gap of $CuGaSe_2$. ESR signals with comparable line shape and g value have been reported previously and were generally assigned to donor- like states in I-III-VI_2 compounds [95, 97]. The Curie type susceptibility up to room temperature indicates these donors states are either not ionized or the donor electron is captured by a deep defect that produces the g =2.003 line in ESR. Irrespective

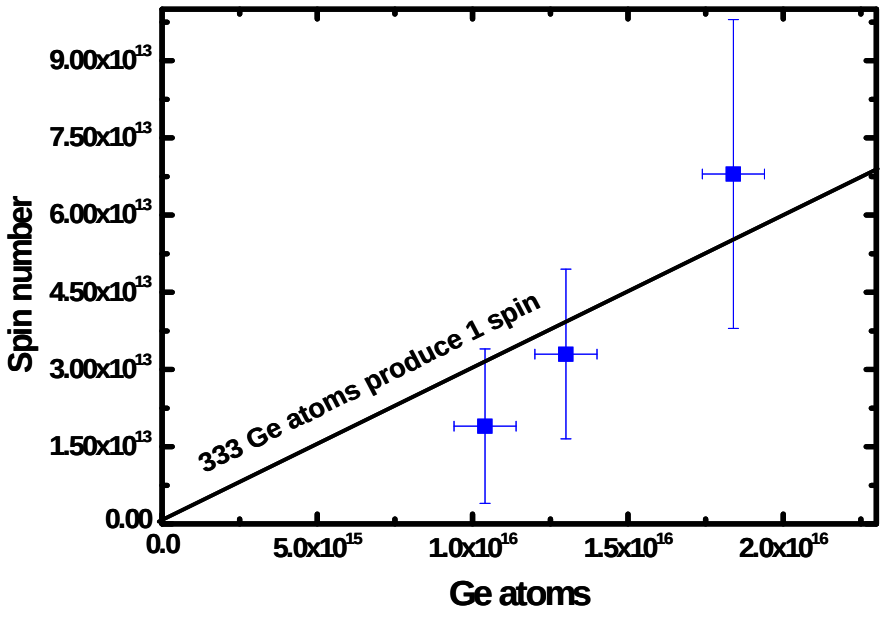
of the microscopic origin of the $g = 2.003$ line it seems that Ge implantation into $CuGaSe_2$ produces a donor state in $CuGaSe_2$; however, the species is not electrically active at room temperature according to the Curie paramagnetism.

6.4 Determination of the spin concentration

Since only Curie paramagnetic centers contribute to the ESR signal at $g = 2.003$, the absolute spin number can be determined by comparison with a sample of known spin concentration. Figure 6.4 (a) displays the dependence of the intensity of the ESR resonance at $g = 2.003$ for different Ge concentrations. It is noticeable that the increase of Ge concentration also induces an increase of the ESR signal, revealing a linear relationship between the $g = 2.003$ line and the Ge content. The spin number ΔN^{Curie} of all the doped films has been determined from the temperature dependence of χ_0 and plotted as a function of Ge atoms estimated from the SNMS measurements, and is displayed in figure 6.4 (b)



(a)



(b)

Figure 6.4 : *(a) Ge concentration dependence of the ESR signal at g =2.003 and T= 5K. (b) spin number determined from the ESR spectra at T = 5K as a function of Ge atoms. The error bars indicates the relative uncertainties.*

The total number of paramagnetic centres induced by Ge implantation is only 0.3 % of the total number of implanted Ge atoms, indicating that not only Ge atoms may contribute to the ESR line $g = 2.003$.

6.5 Concluding remarks

The microscopic origin of the Curie paramagnetism of $CuGaSe_2$: Ge could not be resolved, since the total number of paramagnetic centers induced by Ge implantation in the different films under study was shown to be only 0.3% of the total number of implanted Ge atoms by the implantation treatment as determined by SNMS. However, the identity of the ESR signal led us to the conclusion that we are in the presence of donor states. No indication of delocalized charge carriers is found in ESR due to the fact that no Pauli paramagnetism is observed. Moreover, due to the high value of the spin- orbit splitting of the valence band in $CuGaSe_2$ ($\Delta_{so} = 0.23$ eV) [63], the g- value of free electrons in $CuGaSe_2$ is expected to be around $g = 0.7$ [99]. Therefore, the Curie paramagnetism can be explained by the fact that either the donor electrons remain bound even at T = 300K or they are trapped by a deep defect. The donor is expected not to be electrically active at room temperature because the ESR signal is observed without change of the ESR line shape in the whole temperature range investigated. These results are in good agreement with the phenomenological doping

pinning rule [38], that predicts a self- compensation of the $CuGaSe_2$, when donor states are introduced and this explain well the pinning of the Fermi level towards the valance band edge through the incorporation of donors within the band gap of $CuGaSe_2$.