Mn5Ge3C0.6/Ge(111) Schottky contacts tuned by a n-type ultra-shallow doping layer
Matthieu Petit, Ryoma Hayakawa, Yutaka Wakayama, Vinh Le Thanh, Lisa Michez

To cite this version:
Mn$_5$Ge$_3$C$_{0.6}$/Ge(111) Schottky contacts tuned by a n-type ultra-shallow doping layer

Matthieu Petit$^1$, Ryoma Hayakawa$^2$, Yutaka Wakayama$^2$, Vinh Le Thanh$^1$, Lisa Michez$^1$

$^1$ Aix-Marseille Université, CNRS, CINaM UMR 7325, 13288, Marseille, France
$^2$ International Center for Materials Nanoarchitectonics (WPI-MANA), National Institute for Materials Science, 1-1 Namiki, Tsukuba 305-0044, Japan

E-mail: matthieu.petit@univ-amu.fr

Abstract. Mn$_5$Ge$_3$C$_x$ compound is of great interest for spintronics applications. The various parameters of Au/Mn$_5$Ge$_3$C$_{0.6}$/Ge(111) and Au/Mn$_5$Ge$_3$C$_{0.6}$/δ-doped Ge(111) Schottky diodes were measured in the temperature range of 30-300 K by using current-voltage and capacitance-voltage techniques. The Schottky barrier heights and ideality factors were found to be temperature dependent. These anomaly behaviours were explained by Schottky barriers inhomogeneities and interpreted by means of Gaussian distributions model of the Schottky barrier heights. Following this approach we show that the Mn$_5$Ge$_3$C$_{0.6}$/Ge contact is described with a single Gaussian distribution and a conduction mechanism mainly based on the thermoionic emission. On the other hand the Mn$_5$Ge$_3$C$_{0.6}$/δ-doped Ge contact is depicted with two Gaussian distributions according to the temperature and a thermionic-field emission process. The differences between the two types of contacts are discussed according to the distinctive features of the growth of heavily doped germanium thin films.

PACS numbers: 73.30.+y, 61.72.uf, 61.72.uj, 73.40.-c, 73.40.Gk, 85.75.-d

Keywords: Mn$_5$Ge$_3$, Mn$_5$Ge$_3$C, Germanium, δ-doping, Schottky diodes, Schottky barrier anomalies, Spin injection, Molecular beam epitaxy, Reactive deposition epitaxy
1. Introduction

The rapid evolution of electronics results partly in scaling down the device size. But as device miniaturization reaches technological limits, alternative technologies need to be developed and electronics based on the control and the manipulation of spin degree of freedom of charge carriers in semiconductors holds great promises. This new kind of electronics requires an efficient electrical injection of spin-polarized electrons from a ferromagnet into the conduction band of a semiconductor as well as a subsequent spin-polarized detection. Therefore developing suitable materials for electrical spin injection in group-IV semiconductors is a key step toward the full integration of spintronic devices into the semiconductor technology as pinpointed by the International Technology Roadmap for Semiconductor in the "Emerging Research Materials Difficult Challenges 2013-2020" [1].

Two main ways have been explored in order to inject spin-polarized current into silicon or germanium. Firstly, ferromagnetic metal (FM) such as Co, Fe or Ni have been considered. Spin-polarized carriers tunnel from the metal to the semiconductor through an insulator or a Schottky barrier [2]. However most ferromagnetic metals react with Si and Ge to form non-ferromagnetic interfacial silicides or germanides. It is also not trivial to obtain epitaxial growth of an oxide between Ge (or Si) and a ferromagnetic metal. The other possibility is to use heterostructures of semiconductors and ferromagnetic semiconductors. But to date no semiconductor showing a ferromagnetic order up to room temperature can be obtained in a reproducible manner.

In this context, Mn$_5$Ge$_3$ and Ge are potentially interesting. First of all, Ge is gaining a strong interest in the spintronics field due to its large spin diffusion length and its high carrier mobility. Despite a strong Fermi level pinning (FLP) in metal/Ge contacts [3], electrical spin injection has been demonstrated in Ge with the use of a metal electrode and an oxide tunnel barrier [4, 5, 6, 7]. Moreover, Yamane et al. recently demonstrated in the Fe$_3$Si/Ge(111) system that the FLP effect can be reduced thanks to a high quality structure with an atomically flat interface and they attributed the magnitude of the FLP effect to the presence of disorder at the metal/Ge interface [8]. This underlines the need of a very well controlled and clean interface. Then Mn$_5$Ge$_3$ is an intermetallic compound that can be grown epitaxially on Ge(111) [9, 10]. Its Curie temperature is about 296 K and can be enhanced by carbon doping up to 430 K [11, 12] for Mn$_5$Ge$_3$C$_{0.6}$. Recently, there have been studies from several teams on the Mn$_5$Ge$_3$/Ge(111) contact [13, 14, 15, 16] and specially a report has been published on a large spin accumulation voltage in Mn$_5$Ge$_3$/Ge(111) without an oxide tunnel barrier [17].

Generally speaking, Schottky contacts can be tailored using interfacial layers engineering [18, 19, 20]. More specifically, the Schottky contacts between a ferromagnet electrode and a semiconductor can be tuned by playing with the doping profile at the interface [21]. According to Albrecht et al., the spin injection is deteriorated by the depletion region but can be tailored by a heavily doped layer such as a δ-doped layer [22]. The Schottky barrier parameters i.e. barrier height, depletion region width and contact resistance, are then reduced. Sawano et al. have shown that the contact resistance in a Fe$_3$Si/Ge(111) structure can be substantially reduced when a control Sb δ-doping is introduced in Ge very close to the interface [23] and the combination of high quality Schottky tunnel barrier contact and surface doped layer has led to successful spin accumulation in Fe$_3$Si/Ge(111) [24].

In this framework, we have studied the features of the Au/Mn$_5$Ge$_3$C$_{0.6}$/Ge(111) Schottky contacts by intensity-voltage-temperature (I-V-T) and capacitance-voltage-temperature (C-V-T) electrical measurements, Mn$_5$Ge$_3$C$_{0.6}$ presenting the highest Curie temperature of the Mn$_5$Ge$_3$C$_x$ alloys. The Mn$_5$Ge$_3$C$_{0.6}$ thin films were grown by an uncommon growth process (low temperature reactive deposition epitaxy so-called RDE) we recently developed to improve the quality of the Mn$_5$Ge$_3$C$_x$/Ge(111) interfaces [25]. Furthermore, we concurrently investigated the effect of a heavily n-type δ-doped layer on the interfacial characteristics of Au/Mn$_5$Ge$_3$C$_{0.6}$/Ge(111) Schottky contacts, since such a very thin layer can be a tool to modify these key characteristics regarding the spin injection.

2. Experimental details, devices fabrication and characterisation

Two types of samples were prepared with the following structures (fig.1) from top to bottom: the top contacts are made of a 3 nm Cr bond coat followed by a 100 nm Au layer patterned in 100 × 100 µm$^2$ squares by optical lithography. The contacts size was chosen to avoid edge effects.

The Mn$_5$Ge$_3$C$_{0.6}$ thin films growth on Ge(111) was performed using the RDE method at room temperature. This method has been described and characterised elsewhere and involves the co-deposition of Ge, Mn and C atoms on Ge(111) surface at room temperature [25, 26]. It ensures a very high crystalline quality of the Mn$_5$Ge$_3$C$_x$ thin films and a
sharp interface between these films and the Ge(111) substrates. The n-type Ge(111) substrates are from UMICORE with a resistivity of 1.5 Ω cm$^{-1}$ (doping concentration in the order of $10^{15}$ cm$^{-3}$). On one sample a heavily n-type δ-doped layer was inserted at the top of the Ge(111) substrates prior to the deposition of the Mn$_5$Ge$_3$C$_{0.6}$ thin films (sample B). The target doping concentration of this δ-doped layer is $2 \times 10^{19}$ cm$^{-3}$. The layer is grown by a co-deposition of Ge evaporated from a two-zone heated Knudsen effusion cell and phosphorus atoms produced by a GaP decomposition source (DECO from Dr. Eberl MBE-Komponenten GmbH). The growth parameters were measured with a semiconductor device analyser (Agilent B1500A) in a vacuum chamber at 10$^{-2}$ Pa over a temperature range of 30-300 K through a helium-based closed cycle refrigeration system.

3. Results and discussion

3.1. Extraction of Schottky diodes parameters

The forward I-V characteristics displayed on fig.2a) and b) show typical examples of experimental measurements obtained on the Au/Mn$_5$Ge$_3$C$_{0.6}$ diodes respectively without and with the presence of a n-type δ-doped layer.

A gradual shift of the I-V curves towards higher voltages is observed with the decrease of the temperature for both samples. This indicates that the transport mechanism is thermally assisted and not pure tunnelling. This thermally assisted transport was observed in previous studies of Mn$_5$Ge$_3$/Ge(111) Schottky contacts without carbon doping [15, 17, 28]. On fig.2b) two behaviours can be clearly seen through the two linear regions with different slopes of the semi-logarithmic curves. This point will be discussed later. An example of C-V measurements from both samples is given in fig.2c) at one temperature for clarity. From these measurements we extracted numerically the C-V profiles $N_{CV}$ (eq.1) so as to get a confirmation on an electrical level of the effect of the δ-doped layer [29, 30]:

$$N_{CV} = \frac{C^3}{q\epsilon_s} \frac{dV}{dC}$$

(1)

where $q$ is the electron charge and $\epsilon_s$ the permittivity of the semiconductor. The sample without the δ-layer presents a rather flat profile with a mean value of about $1.4 \times 10^{15}$ cm$^{-3}$ consistent with the manufacturer specifications of the Ge wafer and the sample with the δ-doped layer exhibits the same flat profile except near the interface where the doping concentration increases to about $3 \times 10^{19}$ cm$^{-3}$.

This is in agreement with our previous results and the consideration on the difference between dopant concentrations evaluated by chemical or electrical measurements [27, 31].

To begin our analyses on the Schottky contacts we assumed a thermionic emission (TE) conduction mechanism expressed by the following equation [32]:

$$I = I_s \left\{ \exp \left[ \frac{q(V - IR_s)}{nk_BT} \right] - 1 \right\}$$

(2)

where $k_B$ the Boltzmann constant, $n$ the ideality factor, $R_s$ is the series resistance and $I_s$ the saturation current which is given by:

$$I_s = AA^*T^2 \exp \left( \frac{-q\Phi_{IV}}{k_BT} \right)$$

(3)
\( A \) is the diode area, \( A^* \) is the effective Richardson constant and \( \Phi_{IV} \) is the zero bias Schottky barrier height (SBH). Several methods can be used to determine the Schottky diode parameters. Based on the review written by Olikh et al., our choice fell on the Gromov method [33, 34]. This method allows to find the parameters by a fitting procedure of the I-V curves.

According to this one, \( R_s \) varied from 3500 \( \Omega \) at 30 K to 98 \( \Omega \) at 300 K for the sample without the \( \delta \)-doped layer and from 330 \( \Omega \) at 30 K to 125 \( \Omega \) at 300 K for the sample with the \( \delta \)-doped layer which is in agreement with the low-resistivity Ohmic contacts obtained by \( \delta \)-doping technique in ref.[23]. The evolution of \( \Phi_{IV} \) and the ideality factor \( n \) versus temperature is plotted on fig.3 for both sets of sample: without (a) sample A) and with (b) sample B) a \( \delta \)-doped layer.

These figures show a dependence of \( \Phi_{IV} \) and \( n \) with the temperature especially below 120 K: \( n \) decreases with temperature whereas \( \Phi_{IV} \) increases. The \( \delta \)-doped layer seems to reduce the value of \( \Phi_{IV} \) over the whole temperature range and to strongly affect the value of the ideality factor. We have also determined the SBH from the C-V data (\( \Phi_{CV} \)) by using the \( 1/C^2 \) versus bias voltage graph [35, 32]. Typical examples of such graphs are presented in fig.2c) and show a linear relationship between \( 1/C^2 \) and the applied voltage. The C-V characteristics do not depend on frequency between 10kHz and 1MHz (not shown here) and hysteresis are not observed with forward and reverse bias voltage. Thus there is no significant amount of deep levels within the space charge region [36, 37] and no trapped charge. The values of \( \Phi_{CV} \) are displayed in fig.3c). We observed a decrease of the SBH with the increase of the temperature in a similar trend of the bandgap (continuous black line on fig.3c) calculated from ref.[38, 39]) unlike \( \Phi_{IV} \) versus T. Moreover \( \Phi_{CV} \) of the sample with a \( \delta \)-doped layer is lower than the sample without and consequently the depletion lengths \( W \) inferred from \( \Phi_{CV} \) in fig.3d) are shorter with the presence of a \( \delta \)-doped layer in agreement with previous works [22, 23]. This last point is particularly interesting in the context of the spin injection since the depletion region is basically a region of rather high resistivity which has been proved to be detrimental to the spin polarization [22]. The SBH values from this work and literature coming from I-V and C-V are summarized in table 1. Regarding the conflicting behaviour issuing from the evolution of \( \Phi_{IV} \) and \( \Phi_{CV} \) versus the temperature, it has been already reported for other metal-semiconductor junctions. The SBH of an ideal metal-semiconductor junction is expecting to decrease with the increase of the temperature. The discrepancy comes from spatially inhomogeneous barriers which can be described by Gaussian or multiple Gaussian distributions of the SBH (as discussed in the next part). These inhomogeneities mainly affect the I-V data that rather probe local electrical properties since the current is impacted by local patches of low and high resistivity, whereas the capacitances of the Schottky contacts depends only on the mean value of the barrier distribution [37, 40, 41].

### 3.2. Schottky contacts inhomogeneities: temperature dependence of the Schottky diodes parameters

The reliance on temperature of the SBH and ideality factor \( n \) is a common “abnormality” - the so-called \( T_0 \) anomaly- of the Schottky contacts behaviours which is not described by the TE theory. Many forms of temperature dependence exist and have been reported in literature [37, 40, 42]. These phenomena are explained by SBH inhomogeneities: the contacts between metal and semiconductor are not ideal, which means that there are some unavoidable fluctuations of the SBH on the whole area of the electric contact [43, 44]. The fluctuations can be modelled by several

![Figure 3](image-url)
sub-areas having each a barrier height. Thus to go deeper in the analysis of our I-V results, we will consider a multiple Gaussian distribution of the SBH values to describe the spatially inhomogeneities of the Schottky contacts according to the temperature range. The temperature dependence of the barrier height of such contacts is thus written as follow [44, 45, 46, 47]:

\[
\Phi_{IV - i} = \Phi_{IV - i} - \frac{q \sigma_i^2}{2k_B T_i}
\]  

(4)

Here $\Phi_{IV - i}$ and $\sigma_i$ stand for the mean barrier height and standard deviation of each barrier distributions $i$. The estimations of $\sigma_i$ are calculated by fitting linearly the plots of $\Phi_{IV}$ versus $\frac{q}{2k_B T}$ (not shown here) for the samples with and without the $\delta$-doped layer. The plot of $\Phi_{IV}$ versus $\frac{q}{2k_B T}$ of the sample without the $\delta$-doped layer exhibits only one linear region which means that the Schottky contact can be described with only one Gaussian distribution. On the contrary in the case of the sample with the $\delta$-doped layer, the $\Phi_{IV}$ versus $\frac{q}{2k_B T}$ plot shows two linear regions transitioning around 120 K. It means that the contact of this sample is characterised with two Gaussian distributions: $\Phi_{IV}$ and $\sigma$ present different values according to the temperature range. The results are displayed on table 2.

Table 2. Results of the linear fits of $\Phi_{IV}$ versus $\frac{q}{2k_B T}$ for the samples with and without the $\delta$-doped layer assuming a multi-Gaussian distributions of the SBH. $R_i^2$ are the correlation coefficients of the fits.

<table>
<thead>
<tr>
<th>$\delta$-doped layer</th>
<th>without</th>
<th>with</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gaussian distribution 1</td>
<td>whole T range</td>
<td>above 120 K</td>
</tr>
<tr>
<td>$\Phi_{IV - i}$ (eV)</td>
<td>0.45</td>
<td>0.45</td>
</tr>
<tr>
<td>$\sigma_1$ (V)</td>
<td>0.050</td>
<td>0.067</td>
</tr>
<tr>
<td>$R_i^2$</td>
<td>0.91</td>
<td>0.94</td>
</tr>
<tr>
<td>Gaussian distribution 2</td>
<td>below 120 K</td>
<td></td>
</tr>
<tr>
<td>$\Phi_{IV - i}$ (eV)</td>
<td>-</td>
<td>0.31</td>
</tr>
<tr>
<td>$\sigma_2$ (V)</td>
<td>-</td>
<td>0.036</td>
</tr>
<tr>
<td>$R_i^2$</td>
<td>-</td>
<td>0.95</td>
</tr>
</tbody>
</table>

To check the results of the multi-Gaussian distribution model of the SBH, we look at the Richardson plot (fig.4): the plot $\ln \left( \frac{I_s}{T^2} \right) = f \left( \frac{1}{T} \right)$ coming from eq.3 should be linear in the case of an homogeneous Schottky contact. In the case of the Gaussian distributions of the SBH, the linearisation of the Richardson plot is obtained by subtracting $\frac{q^2}{2k_B T^2} \sigma_i^2$ to $\ln \left( \frac{I_s}{T^2} \right)$ according to the temperature ranges $T_i$. It gives the following equation:

\[
\ln \left( \frac{I_s}{T^2} \right) = \ln A^* - \frac{q}{k_B T_i} \Phi_{IV - i} + \frac{q^2}{2k_B T_i^2} \sigma_i^2
\]  

(5)

The good correlation coefficients of the linear fits confirm the validity of the chosen model. To explain the presence of inhomogeneities at the metal-semiconductor interface, we can look into more details the growth process of the Mn$_5$Ge$_3$C$_{0.6}$/Ge(111) thin films. We have shown that there is an interfacial layer of about 2-3 nm thick between the Ge(111) substrate and the Mn$_5$Ge$_3$C$_{0.6}$ films involved in the stress relaxation of the latter (lattice mismatch between Ge(111) and Mn$_5$Ge$_3$ around 3.7 %) [25]. On a magnetic point...
of view, this interfacial layer could be related to the ferromagnetic dead layer highlighted in ref.[48]. The properties of this layer are still under investigations and seem to be strongly influenced by the growth conditions [49]. Moreover the difference between the two samples in term of Gaussian distributions (especially below 120K) may arise from the heavily doped phosphorous δ-layer. As we mentioned earlier, this layer is grown by a co-deposition of Ge and P at low substrate temperature (523 K) according to our previous work where we demonstrated that the sticking coefficient of P₂ is the determining parameter to reach a high doping level in Germanium [27]. No thermal annealing were performed right after the growth of the δ-doped layer. Post growth annealing is indeed not compulsory to achieve high activation of dopants [50]. Moreover it allows to avoid any further segregation of phosphorous atoms which may induce additional inhomogeneities at the interface. However P doped Ge films grown at low temperature usually contain a rather high density of point defects such as vacancies and interstitials [51, 52]. The surface segregation of P atoms has been reported to achieve high activation of dopants [50]. Moreover it might be possible that the δ-doped layer presents some amount of these point defects entailing the observed modification in the SBH distributions compared to the sample without this δ-doped layer.

3.3. Temperature dependences and conduction mechanisms

The field emission and thermoionic-field emission are generally considered as the conduction mechanisms ruling the excess current through the Schottky contacts in the highly doped semiconductors. In the present case of a very thin high n-doped layer, the tunnelling conduction has been proved to be dominant in the Fe₃Si/Ge Schottky contact [23]. In order to get an insight in the type of conduction taking place in our devices, we have analysed the T₀ anomaly by drawing the \( \frac{n k_B T}{q} \) vs \( \frac{k_B T}{q} \) plots for the sample with and without the δ-doped layer (cf. fig.5).

According to these graphs, we have decided to fit the results from the sample without a δ-doped layer with a simple linear relationship as described in the so-called T₀ effect meaning that the conduction mechanism is mainly supported by TE [53, 42]. The SBH inhomogeneities consisting of low and high-SBH contact regions as brought out by the Gaussian distribution explain this behaviour [40]. We should notice that in our case the slope of our fit is slightly higher than unity in contrary of a pure T₀ effect. This is in agreement with the evolution of the ideality factor of this sample: \( n \) depends on the temperature from 30 to 120 K and then is almost constant with a value around 3.8 (cf fig.3a)). This sample presents a mixed trend between a temperature independent and greater than unity ideality factor and the T₀ effect behaviours.

Regarding the sample with a δ-doped layer, the data were fitted using the TFE model [54, 55]:

\[
\frac{n k_B T}{q} = \frac{E_{00}}{1 - \beta \coth \left( \frac{qE_{00}}{k_B T} \right)}
\]  

(6)

In this expression, \( E_{00} \) is a characteristic energy of the semiconductor relative to the tunnel effect transmission probability and \( \beta \) is the bias dependence of the barrier height. The theoretical value of \( E_{00} \) is given by:

\[
E_{00} = \frac{\hbar}{4\pi} \sqrt{\frac{N_D}{m^*\epsilon_s}}
\]  

(7)

where \( N_D \) is the free carriers concentration and \( m^* \) the effective mass of the free carriers. In our case, this theoretical value is equal to about 7.6 meV.
The results of the fit of the experimental data of fig.5 with eq.6 are given in table 3. The experimental value of $E_0$ is higher than the theoretical one. Such an observation was already reported in ref.[55]. A proposed explanation is an increase of the density of states at the metal-semiconductor interface. This is the case in the sample with the $\delta$-doped layer where the interfacial states density $N_{ss}$ is around $5 \times 10^{13} \text{ eV}^{-1}\text{cm}^{-2}$ compared to the sample without the doped layer where $N_{ss} = 3 \times 10^{12} \text{ eV}^{-1}\text{cm}^{-2}$.

These comments and the nuances on the relationships between the observed temperature dependence and the TFE mechanism detailed in ref.[40] do not allow to conclude that the TFE theory fully describe the sample with the $\delta$-doped layer. However they are consistent with the presence of low-SBH patches as determined by the Gaussian distributions model of the SBH.

4. Conclusion

The $\text{Mn}_5\text{Ge}_3\text{C}_0.6/\text{Ge}$ and n-$\delta$-doped $\text{Mn}_5\text{Ge}_3\text{C}_0.6/\text{Ge}$ Schottky contacts have been studied as a function of temperature in the range of 30 to 300 K. The $\text{Mn}_5\text{Ge}_3\text{C}_0.6$ thin films were grown by a method based on reactive deposition epitaxy recently developed to improve the quality of the interface between Ge(111) and $\text{Mn}_5\text{Ge}_3\text{C}_x$. The effect of a heavy P $\delta$-doped layer at the interface on the Schottky contact parameters has also been analysed since the use of a $\delta$-doped layer may allow to tune the characteristics of the Schottky contacts. We have shown that the depletion length $W$ is decreased by the added $\delta$-doped layer. This point is interesting for the spin injection. The barrier heights and ideality factors of these $\text{Mn}_5\text{Ge}_3\text{C}_0.6/\text{Ge}$ and $\delta$-doped $\text{Mn}_5\text{Ge}_3\text{C}_0.6/\text{Ge}$ Schottky contacts were found to be temperature dependent. Assuming spatially inhomogeneous contacts, we used a model based on Gaussian distributions of the barrier heights to interpret the experimental data. A deeper analysis of the $T_0$ anomalies revealed that the $\text{Mn}_5\text{Ge}_3\text{C}_0.6/\text{Ge}$ Schottky contact is mainly controlled by TE conduction and that the $\delta$-doped $\text{Mn}_5\text{Ge}_3\text{C}_0.6/\text{Ge}$ contact may be rather governed by TFE mechanism. These differences between the contacts with and without the $\delta$-doped layer were explained in the light of the growth of this heavy phosphorous doped Ge layer: phosphorous atoms are known to segregate at the surface of the Ge film even at low temperature and then deteriorate the electrical properties of the interface between the metal and the semiconductor. This drawback could be easily overcome by the growth of ultra thin silicon overlayer on top of the $\delta$-doped germanium layer as recently demonstrated in ref.[56] while checking the effect of this extra layer on the spin injection.

Acknowledgements

Parts of this work has been carried out thanks to the support of the A*MIDEX project (ANR-11-IDEX-0001-02) funded by the "Investissements d'Avenir" French Government program, managed by the French National Research Agency (ANR).

References


Mn$_5$Ge$_3$C$_{0.6}$/Ge(111) Schottky contacts tuned by a n-type ultra-shallow doping layer