Spin-polarized tunneling as a probe of (Ga,Mn)As electronic properties

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We present magnetic and tunnel transport properties of (Ga,Mn)As/(In,Ga)As/(Ga,Mn)As structure before and after adequate annealing procedure. The conjugate increase of magnetization and tunnel magnetoresistance obtained after annealing is shown to be associated to the increase of both exchange energy $\Delta_{\text{exch}}$ and hole concentration by reduction of the Mn interstitial atom in the top magnetic electrode. Through a 6x6 band k.p model, we established general phase diagrams of tunneling magnetoresistance (TMR) and tunneling anisotropic magnetoresistance (TAMR) vs. (Ga,Mn)As Fermi energy ($E_F$) and spin-splitting parameter ($B_C$). This allows to give a rough estimation of the exchange energy $\Delta_{\text{exch}}=6B_C \approx 120$ meV and hole concentration $p \approx 1.10^{20}$ cm$^{-3}$ of (Ga,Mn)As and beyond gives the general trend of TMR and TAMR vs. the selected hole band involved in the tunneling transport.

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I. INTRODUCTION

In the field of spintronics, the $p$-type ferromagnetic semiconductor (Ga,Mn)As offers many advantages to study tunnel magnetotransport properties when used as an electrode. The complexity of the transport mechanisms associated with spin-orbit coupled states make this material a powerful means for finding novel effects and provides new challenges for theoretical understandings. This includes tunnel magnetoresistance (TMR) across single and double barriers, tunnel anisotropic magnetoresistance (TAMR) Coulomb blockade anisotropic magnetoresistance and current induced magnetization switching. However one of the main limitation of this $p$ type material for spintronic integration is the relatively low Curie temperature. Through low temperature annealing treatment after growth, Curie temperatures of 173 K can be obtained. Elimination of interstitial manganese atoms which are double donors and which couple antiferromagnetically with the manganese atom in substitutional position, is mainly invoked. These atoms diffuse towards the surface to form either a MnO$_2$ or a MnN$_2$ layer, depending on annealing conditions.

In this paper we describe the effect of annealing on the magnetic and electric properties of a (Ga,Mn)As/(In,Ga)As/(Ga,Mn)As tunnel junction. We have focused our report on this single structure even though other junctions with different Mn concentrations and ferromagnetic layer thicknesses were studied, leading to the same general conclusion. In the first part we detail the effect of annealing on magnetization measurements and confirm observations made on a (Ga,Mn)As trilayer structure with a GaAs barrier. The second part presents the results obtained on junctions fabricated by optical lithography and describes the behaviour of Resistance Area (R.A) product, Tunnel Magnetoresistance (TMR) and Tunnel Anisotropic Magnetoresistance (TAMR) through annealing. In the last part, a general interpretation of the data behaviour from both magnetic and electric measurements, is given through a 6x6 band $k.p$ model of the tunneling transport. Two important parameters are identified, the Fermi energy and the spin splitting parameter $B_C$ introduced in the framework of the Zener model in the mean-field approach.

II. EXPERIMENTAL RESULTS

(Ga$_{0.926}$Mn$_{0.074}$As (80nm)/ In$_{0.25}$Ga$_{0.75}$As (6nm)/ Ga$_{0.926}$Mn$_{0.074}$As (15nm) structure is grown by molecular beam epitaxy at 250 °C on a $p$-doped GaAs buffer layer ($p \approx 2.10^{19}$ cm$^{-3}$). Annealing treatment has been realized at 250 °C in a nitrogen atmosphere during 1 hour. The annealing was performed on a whole piece of 5x5 mm$^2$ for magnetic measurements whereas realised on patterned junctions for electrical experiments.

Figure 1 presents magnetization behaviour before and after annealing by SQUID (Superconducting Quantum Interference Device) measurements. The two step magnetization reversal along [100] axis at 10 K is due to the consecutive reversal of the two magnetic layers [Fig. [1]a]. As a function of annealing, three important characteristics, consistent with the reduction of Mn interstitials in the top magnetic layer, can be extracted from those measurements: a large decrease of the coercivity $H_C$ as well as an increase of the magnetic moment $M_S$ and of the Curie temperature $T_C$. Concerning the variation of the $H_C$, magnetization study pointed out that this decrease may be due to an elimination of interstitial manganese (double donors) pinning center. The resulting increase of the carrier concentration may also contribute to the decrease of the anisotropy field. Considering that only the top layer is affected by annealing, through its linear
dependence on the magnetization saturation value, the spin splitting parameter increases from 17 meV (before annealing) to 24 meV (after annealing). The values of the spin splitting were estimated through the relationship \( B_G = \frac{2 M}{g \mu_B} \) derived from the mean field theory, where \( A_F \) is the Fermi Liquid parameter and \( \beta \) the p-d exchange integral.\(^\text{14}\)

The observed Curie temperature are in good agreement with those found on thicker magnetic layers confirming that layer width larger than 50 nm should still have a high concentration of manganese interstitials.\(^\text{10,16}\) In the present case, the Curie temperature goes from 55 K to 122 K (Fig. \(1\)b). Due to the higher magnetic moment of the top layer, the behaviour of the thin bottom layer is hidden, supporting the results that only the top layer properties change. A further confirmation that annealing does not act on the bottom layer comes from Auger measurements, not presented here. A strong manganese accumulation at the top of the surface is measured, whereas no obvious change in the bottom layer is observed, already put forward by Chiba et al.\(^\text{13}\) Capping (Ga,Mn)As layer by a simple GaAs layer which width exceeds 5 nm, does not improve the Curie temperature of the simple magnetic layer\(^\text{15}\) and does though support our results. The formation of a p-n junction avoiding the migration of interstitial n-type manganese has been suggested.\(^\text{12}\)

Magnetic tunnel junctions have been patterned by optical lithography (size of the junctions were between 8 and 128 \( \mu m^2 \)). With standard dc technique the resistance of the junctions is measured at 3K and at low bias (1 mV) in the CPP (Current Perpendicular to Plane) regime. Non-linear I(V) curve indicates that a 6 nm (In,Ga)As layer still acts as a barrier.\(^\text{18}\) The reason is on the one hand that the Mn acceptor level in GaAs leads to a positive band offset in (Ga,Mn)As compared to GaAs. On the other hand the well-known As antisites incorporated during the low growth process should probably govern the pinning of the Fermi level and a higher barrier than the simple Mn acceptor state may be expected. In figure \(2\)a we note an increase of TMR from 30% before annealing to 120% after annealing on a 128 \( \mu m^2 \) junction (along [100] direction) while R.A product decreases from 0.047 to 0.003 \( \Omega \cdot cm^2 \). Lowering R.A. product should be related to a change in the Fermi energy which involve a reduction of the barrier height or the barrier width and then must be associated to an increase of the hole concentration. In addition, as already observed on magnetic properties, the coercive field of the top magnetic layers changes after annealing: the difference of those values between magnetic and transport measurements is related to size effects. The same behaviour has been observed on all 4 measured junctions (Fig. \(2\)b): Whereas TMR values lay between 30% and 90% before annealing, an homogenization of the values occurs after annealing where TMR ranges between 110% and 130%. No asymmetry of TMR between positive and negative applied bias has been measured after annealing.

However, we must emphasize that magnetic properties derive from the whole magnetic layers (volume effect), whereas electric properties should mainly depend on the interfaces between the tunnel barrier and the electrodes. It results that evaluating the change of the electronic properties for each magnetic layers from transport measurements appears more complex than in the case of magnetic experiments. Nevertheless, some conclusions can be drawn from TMR measurements vs. temperature, taking into account that the elementary process is a spin-conservative direct tunneling, i.e. the evolution of TMR with temperature is directly linked to the effective
carrier spin polarization of the ferromagnetic layer\textsuperscript{19}.
We note that the effective temperature at which TMR cancels remains unchanged after annealing [Fig 2(c)]. This feature comes from the magnetic properties of the bottom electrode which are not modified after annealing (T\textsubscript{C}~\textasciitilde 55 K). The drop of TMR around 15 K before and after annealing is related to the quick variation of the coercive field of the thin magnetic layer as a function of the temperature.\textsuperscript{20}

On the other hand, how behaves the tunnel anisotropic magnetoresistance (TAMR)? TAMR generally traduces a variation of resistance \textit{vs}. the crystalline orientation of the electrode magnetization. In this case, this originates from the anisotropy of the valence band of (Ga,Mn)As. Careful attention was paid on the resistance difference when the magnetization is aligned along [100] (in plane magnetization) or [001] (out of plane magnetization) which leads to maximum TAMR effect in our samples. In a saturating field of 6 kOe variations are almost equal to 10-15% before and after annealing [Fig. 2(d)], in good agreement with experiments obtained on a ZnSe barrier.\textsuperscript{21}

When driving experiments in the plane of the layer resistance variations as small as 4% were recorded.

III. THEORETICAL MODEL

Our calculations of the transmission coefficient are based on the multiband transfer matrix technique developed in details by Pethukov et al.\textsuperscript{22,23} Brey et al.\textsuperscript{22} and Krstajic et al.\textsuperscript{22,24} and applied to the hole 6\times6 valence band \textit{k.p} Hamiltonian \(H_h\). Added to the Kohn-Luttinger kinetic Hamiltonian, this includes a \(p-d\) exchange term introduced by the interaction between the localized Mn magnetization and the holes derived in the mean-field approximation thus giving:

\[
H_h = -(\gamma_1 + 4\gamma_2)k^2 + 6\gamma_2 \sum_{\alpha} L^2_{\alpha} k^2_{\alpha} + 6\gamma_3 \sum_{\alpha \neq \beta} (L_{\alpha} L_{\beta} + L_{\beta} L_{\alpha})k_{\alpha}k_{\beta} + \lambda_\alpha \nabla(\vec{S}^2) + 6B_G\vec{m} \cdot \vec{S} \tag{1}
\]

equivalent to the one proposed by Dietl et al.\textsuperscript{14} and Abolfarth et al.\textsuperscript{25}. Here, \(\alpha = \{x, y, z\}\), \(L_{\alpha}\) are \(l = 1\) angular momentum operators, \(\vec{S}\) is the vectorial spin operator, \(\vec{m}\) the unit magnetization vector and \(\gamma_1\) are Luttinger parameters of the host semiconductor GaAs. \(6B_G\) represents the spin-splitting between the heavy holes at the \(\Gamma_8\) point like originally introduced by Dietl et al.\textsuperscript{14}. We do not take explicitly into account the stress hamiltonian which is shown to give the same qualitative conclusions.

To derive the transmission coefficient, the boundary conditions to match at each interface are:\textsuperscript{22}

\(i)\) the continuity of the 6 components of the envelope function according to \(\psi_{n+}^+ + \sum_{\alpha} r_{n,\alpha} \psi_{n,\alpha}^- = \sum_{n'} t_{n,n'} \psi_{n,\alpha}^+\), where the subscript \(t_{n,n'}\) \((r_{n,\alpha})\) refer to the respective transmission (reflection) amplitude from \textit{incident} \((n)\), \textit{reflected} \((\vec{n})\) and \textit{transmitted} \((n')\) waves together with

\(ii)\) the continuity of the 6 components of the current wavevector according to \(\hat{J}_{\psi_{n+}^+} + \sum_{\alpha} r_{n,\alpha} \hat{J}_{\psi_{n,\alpha}^-} = \sum_{n'} t_{n,n'} \hat{J}_{\psi_{n,\alpha}^+}\), where, in the \textit{k.p} approach, the current operator in the \(z\) direction writes \(\hat{J} = \frac{1}{\hbar} \frac{\partial H}{\partial \hat{z}}\).

Concerning the heterostructure itself, the valence band offset (VBO), \(d_B\), between (Ga,Mn)As and (In,Ga)As fixes the effective barrier height \(\phi\) according to \(d_B = E_F + \phi\) where \(E_F \approx -0.18\) eV is the Fermi level within (Ga,Mn)As calculated from the top of the (Ga,Mn)As valence band [Inset Fig 3]. On figure 3 we present the calculated R.A product vs. the respective valence band offset using standard Landauer formula of conductance for 6 nm GaAs and In\(_{0.25}\)Ga\(_{0.75}\)As barriers. Although the VBO between Ga\(_{0.926}\)Mn\(_{0.074}\)As and In\(_{0.25}\)Ga\(_{0.75}\)As is still unknown, recent photoemission spectra determined the barrier height \(\phi\) between (Ga,Mn)As and GaAs to 450 meV\textsuperscript{26} in agreement with our \textit{k.p} model considering a R.A product approaching \(\sim 10^{-3}\) \(\Omega\text{cm}^2\) [Fig. 3] and like obtained experimentally by Chiba et al.\textsuperscript{27} The relative small band offset between valence band of GaAs and (In,Ga)As inferior to 50 meV\textsuperscript{28} makes then such value of \(\phi \sim 450\) meV a plausible order of magnitude for the effective barrier height for In\(_{0.25}\)Ga\(_{0.75}\)As matching with the R.A product after annealing. However, in the present case, the real value of \(\phi\) may vary depending on:

\(i)\) the nature and density of the dangling bonds at the interfaces promoted by the low-temperature growth procedure.\textsuperscript{27}
We can point out that a change of TAMR \( n=2 \) and \( n=3 \) subbands are dominant in the tunneling with the results that TAMR becomes positive when argument is reversed for the second and third subbands then a larger transmission through the barrier.

The first subband clearly gives a negative possible change of sign for TAMR on crossing the third subband. The dominant heavy hole character of such band, an in-plane contribution to TAMR. This originates from the pre-conjugate TMR and TAMR values obtained before and after annealing [Fig.4]. A good qualitative agreement can be found for TMR values as well as theoretically established through tight-binding treatment. Reducing the hole concentration through hydrogenation technique should give the possibility to probe this possible crossover from positive to negative TAMR.

Concerning our own experiments, taking into account conjugate TMR and TAMR values obtained before and after annealing, one can roughly evaluate the projection of the corresponding signals trajectories in the \([E_F, B_G]\) plane followed during annealing [Fig.4]. A good qualitative agreement can be found even though symmetrical junctions were simulated in order to restrict the number of parameters.

Evaluating directly the interfacial spin splitting from the mean field theory appears difficult since the interfacial magnetic properties are hardly accessible. However, when using the estimated \( B_G \) value of the top magnetic electrode (before and after annealing) a good qualitative agreement can be found for TAMR.
and TAMR, as illustrated by the trajectory in figure [1] between point 1 (before annealing) and point 2 (after annealing). A more refined calculation including two different B_G after annealing should be required to draw definite quantitative conclusion.

We are now going to discuss the hole concentration derived from these diagrams. TMR and TAMR values obtained before annealing are well reproduced for a hole concentration approaching 10^{20} cm^{-3}, in good agreement with the one measured for single (Ga,Mn)As layer and already reported. The annealing procedure has for effect to i) remove Mn interstitial atoms, ii) increasing carrier concentration and iii) reduce the effective barrier height even if the valence band position is expected to rise due to an increase of the average exchange energy (B_G). The large reduction of the R.A product together with the increase of TMR are consistent with such assumption. Nevertheless, the hole concentration extracted after annealing from the phase diagram ~1.7 \times 10^{20} cm^{-3} appear to be weak compared to the one reported in the literature and derived from Hall effect measurements. The existence of a possible concentration gradient can be at the origin of such discrepancy. Also can be invoked, a reduction of the hole concentration at the interfaces with the barrier due to a significant charge transfer between p-type (Ga,Mn)As and n-type (In,Ga)As (excess of As antisites).^{25,34}

V. CONCLUSION

In summary we have shown that annealing a (Ga,Mn)As-based tunnel junction mainly affects the properties of the top magnetic layer, ensuring an increase of the effective magnetization and a significant enhancement of the tunnel magnetoresistance. The confrontation between experiments and modelisation performed within a 6x6 band k.p treatment vs. intrinsic (Ga,Mn)As parameters (hole filling, exchange energy) allowed a rough estimation of the average exchange interactions and carrier concentration in (Ga,Mn)As at the interface with the barrier. We point out that while the magnitude of TMR appears very sensitive to both parameters (B_G and E_F), the TAMR variation is limited to several tens of percent but may change sign crossing from upper to lower (Ga,Mn)As subbands. As a final conclusion, we think that this reduced parameter model gives a good qualitative agreement of the tunneling transport and enables to extract the fundamentals of TMR and TAMR processes involving tunnel transport of spin-orbit couple state. In order to go further and draw more quantitative information, a perfect control and knowledge of the carrier density seems to be necessary.

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