From Lab to the Fab: Production of Magnetic Materials for Spintronics Applications

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Materials, more or less sophisticated, are present in our life since several thousand years. Man's intelligence, in the need to improve his life condition, contributed to the evolution of the materials used in our daily life (from the simplest ones like the wood and stone to more complex ones like bronze and iron). The impact of materials in Man's evolution was so strong than we can assert it helped to model civilizations. For instance, in the case of Hittites (18th century before Christ), the improvement of the technique to fabricate very good quality iron made them one of the most advanced and powerful civilizations of the antiquity and helped them to dominate the Mediterranean region **[Hum_04]**. Another example from history: the bronze discovery was due to the insertion of 10% tin (Sn) in copper (Cu) in order to decrease its melting temperature, making easier the elaboration of different objects.

The appreciation of the materials impact in Man's history and evolution was illustrated in the History by naming each era after the material used:
- stone age - 4500 bc
- bronze age - 1700 to 0 bc
- iron age – 1500 bc to 1950 ac

The last era the Iron age is more close to our days. Iron is a material with a lot of applications in our days on different forms. Iron in pure state is a magnetic material very ductile and can be used as compass or as the core of a coil but is susceptible of corrosion. Adding some impurities as C, P (1%) and Cr (10%), changes the mechanical properties of Fe and becomes stronger and it transforms in inoxidable steel.

One particular amazing demonstration of iron workmanship is the famous iron pillar from Delhi in India. The pillar made of forged iron is seven meters tall and has a purity of about 99.2% (quality obtained only in XIX century in Occident), containing only small amounts of sulphur (0.08% S), phosphorus (0.11% P), silicon (0.46% Si), and carbon (0.08% C). This was fabricated by indians in middle of IIIrd century C.E. by using a one-step technique for steel fabrication by doing a mixture of Fe with glass then slowly heated in fire based on wood charcoal and then cooled. This metallurgic curiosity was solved only in 2002 when has been found that the Fe is protected by surface layer of iron hydrogen phosphate. It is speculated that combination of climatic factors, high P and S contents and a large heat capacity helped the inclusion of S and P at the surface. At that time the process of fabrication was not understood and was explained as a purification by fire. But later the process was scientifically explained: during heating the glass was purifying the iron by the impurities and the C and P vas incorporated at the surface. The steel that we use today was discovered by a French metallurgist and geologist Pierre Berthier in 1821 studying the alloys of Fe with Cr. This examples show that the process of fabrication of materials as annealing or incorporating impurities can make a big difference in the materials physical properties opening the way for new applications.

In our days a lot of research work is conducted to improve the materials properties or discover new materials and understand their properties in order to feed our needs in terms of technological applications or to discover interesting phenomena to be understood and valorized.

Today, the new techniques of thin film fabrication (nm thickness) like Molecular Beam Epitaxy or Physical Vapor Deposition (PVD, or sputtering) allowed growing very thin films of magnetic materials, metals or insulators in complicated stacks and made possible to evidence new physical phenomenon like:

- Interfacial perpendicular magnetic anisotropy (PMA) **[Gra_68]**

- Giant MagnetoResistance (GMR) **[Bai_88, Bin_89]**

- Tunnel MagnetoResistance (TMR) **[Moo_95]**

- Oscillatory character of RKKY exchange coupling **[Par_91]**.

All these fascinating phenomena consider the spin of the electron in addition to its charge, associating magnetism and electronic transport in a new research area: the **spin electronics or Spintronics**.

As shown in the paragraph before the fabrications techniques can change and model material. So today as well research laboratories and Industrials R&D and Engineering divisions are focused a lot on new techniques of materials fabrication. Once the process is well developed and understood in the laboratory and meets industry requirements, as cost of manufacturing, it is transferred to mass production and for that the industry need to be prepared with very stable and precise tools. One of the biggest tools manufacturer industrials for electronic materials for semiconductor industry and "***one of the most important U.S. companies you've probably never heard of"*** [Thomas Friedman, *The New York Time],* **is Applied Materials.**

Applied Materials is the number one equipment manufacturer of PVD tools, having the leadership of the metallization over 20 years. This success was possible by dedication of the Applied Engineers and Scientists, to provide a solution for advanced metallization applications by replacing the chemical vapor deposition (CVD) technique with physical vapor deposition (PVD). Applied was already innovating for the CVD tools for example the Precision 5000 CVD tool was the first cluster tool and one of the industry's first single-wafer multi chamber platform. Since the impact that this released platform had on industry, a P5000 is available to be seen in Smithsonian Museum in United States of America. This platform served to the development of the first Applied PVD tool and the CVD reactor was transformed in PVD one, without a success at the beginning because the vacuum was not good enough and affected film growth. But this first attempt to make a PVD tool challenged Applied Scientists and Engineers to improve the vacuum by changing the platform from one load lock chamber to dual load-lock chambers, and the Endura platform was born in 1990 as the first ultra-high vacuum (UHV) production system (10^{-9} torr). Based on these innovations, the Endura system has played an instrumental role in enabling major industry milestones and inflections, including [AMAT]:

- **Scaling aluminum interconnects to sub-1 micron designs**
- **Revolutionary transition to copper dual damascene interconnect**
- **Groundbreaking materials and architectural change in transistors: metal gate and 3D FinFET**

Today the memories industry is searching for a new candidate for non-volatile memories applications. A high density/stable/fast MRAM memory using a tunnel magneto resistance phenomenon discovered in thin magnetic/metal/insulator films, is one of the nonvolatile memory candidates which could be used in different applications and replace the different memories of present times.

Applied Materials is closely following the needs in tools for new technologies by constantly investing in R&D and Engineering of around 1.2 M$. Since this technology requires very thin films of 2A to 200A thick and more than 6 materials the actual single wafer multichamber cluster Endura is no more enough. A multicathode chamber can be a solution to increase the number of materials possible to an industrial tool and not increase the size of the tool. But the difficulty with a multicathode chamber is mostly related to the chamber design in order to have:

- **Good film uniformity on 300mm wafers using smaller targets than the wafer size**
- **Manage the cross contamination between the targets in an industrial elegant way**
- **Manage the particles that can be created by sputtering of different materials in the same chamber, for examples metals have bad adhesion on oxides**

The GMR discovery offered a new concept for magnetic sensor device: the **spin valve [Die_91] which had a huge impact on the HDD industry**. Giving a much improved sensitivity at nanoscale than inductive or even anisotropic magnetoresistance sensors, the spin valves were rapidly integrated in the read/write heads of the hard disk drive (HDD) industry. This allowed a fast increase of the HDD areal density**,** and inspired a new device for industrial applications, the **Magnetic Tunnel Junction**. The evolution from GMR heads to TMR in HDD heads is an example showing that even the film stack is complex can be industrialized giving a hope for the Magnetic Tunnel Junctions integration in MRAM chips.

The magnetic tunnel junctions (MTJ) are spintronic devices having two magnetic thin layers separed by a very thin insulator (oxide) layer so that electrons can pass from one ferromagnetic layer to the other by tunneling. In this case the **spin filtering** effect is dominant compared to spin diffusion and the result is a very high relative resistance variation as a function of the magnetization alignment in the magnetic layers, called Tunnel MagnetoResistance (TMR). This is why MTJ devices have a higher output signal than spin valves, making them very attractive for industrial applications. The difference in the resistance values between the P and AP configuration of the magnetic layers can be used for binary coding so that new recording media applications or logic circuits can be imagined.

In the future, consumer needs for recording media will demand to combine **high access speed, reduced noise, reliability, portability, non-volatility and low power consumption in a smallest as possible chip with high density. For the last one the requirements of the memory industry regarding the memory point size are more aggressive than the** read/write heads of the hard disk drive (HDD) industry, asking for memory points of the size of a transitor today (30nm). Even this requirement on the size makes more difficult the integration of the MTJ in a MRAM chip the advantages of MRAM make it worth it to try.

MRAM is attractive for industrial applications because it could, in principle, replace other kinds of memories and reduce consumption and operation time compared to FLASH (non-volatility) with a unlimited read/write endurance (10^{15} read-write cycles), in addition to those of conventional RAM memories (speed of SRAM). For instance using a MRAM in a computer, data could be loaded directly into the working memory and wouldn't have to juggle between main memory (SRAM) and hard disk. This could make possible instant-on systems and innovate in the computer architecture. Already in 2013 Toshiba showed 80% reduction of energy consumption in the cach memory of an ARM-core based CPU when using an MRAM cach memory compared with an SRAM.

But, even if MRAM writing technique seems the simplest one using an applied field to switch the free layer magnetization, the architecture required is complicated and requires a lot of space for the electrodes that create the magnetic field, making impossible to reach high densities. In addition, Field Induced Magnetic Switching MRAM architectures reach their limits when the cell size is reduced below 100 nm. Decreasing the cell size will increase the current density necessary to produce the switching field and also the write power, the selection errors for writing the memory cells will also increase, as the impact of the thermal fluctuations on the data stability. A 4Mb-MRAM was commercialized by Freescale Motorola (now EverSpin) in 2006 **[Eve_06]** and finds applications in satellite, aerospace, automotive/ telecommunications industries or memory embedded in controllers or printers.

A new physical phenomenon for magnetization switching, the **spin transfer torque switching (STT)** predicted by Slonczewski in 1996 **[Slo_96, Ber_96]** and first measured in spin valves **[Kat_00, Sun_02, Puf_03]** gives the possibility to create a STT-MRAM architecture showing considerable advantages:

- no more addressing errors because only the pillars traversed by the pulse current will be written
- Increasing the memory density, by suppressing write line, enables 1 Transistor-1 MTJ per cell similar to DRAM and makes possible the MTJ cell size reduction.

In the case of nano-magnetic elements with in-plane magnetization, the thermal stability limit is not related to the current induced switching parameters, but to their shape. In materials without preferred in-plane axis for the magnetization (without crystalline anisotropy), a specific elliptical shape is required to stabilize the magnetization along the long in-plane axis in order to minimize the magnetostatic energy. Reducing cell size makes impossible to keep the elliptical shape and to prevent from magnetization curling due to thermal fluctuations. One solution is to define the magnetization direction of the free layer by coupling it to an antiferromagnetic layer (AF). The switching of the free layer is realized by heating the MTJ cell above the blocking temperature of the antiferromagnet. Based on this phenomenon Spintec proposed a new write concept based on thermally-assisted spin transfer torque switching (STT-TAS-MTJ) **[Pre_04, Oun_02, Noz_06, Her_10]**.

Using materials with out-of-plane anisotropy seems to be the only solution to increase the density of the memory chip and enhance the robustness against thermal fluctuations by keep the magnetization along one well-defined axis in MTJ (perpendicular to the film plane) **[Mor_06, Car_08, Yoo_05]**. Furthermore studies **[Man_06, Nak_08]** have shown that STT perpendicular structures may present lower critical switching currents and higher STT efficiency.

PMA can have different origins, either bulk (in hcp CoCrPt, heavy rare earth/transition metal alloys, or FePt $L1_0$ ordered alloys, or interfacial (in Pt/Co, Pd/Co, or Co/Ni multilayers). It has also been observed that a quite large PMA can be induced at the interfaces between the ferromagnetic electrodes and an oxide **[Mon_02, Rod_03]**. One can take advantage of this PMA from the oxide-magnetic electrode interface to fabricate out-of-plane MTJ.

The new out-of-plane MTJ elements are promising for industrial applications pf memories and interesting for fundamental physics. The difficulty here is to find the right materials that can give at the same time the good structural match with the MgO barrier for high TMR and also an important perpendicular anisotropy to keep the magnetization out of plane in 0 field. The most interesting candidates for pMTJ electrodes are FePt L10 materials and the Magnetic Metal/Oxide bilayers. But this material requires fine tuning of the depositing tool. For Magnetic Metal/Oxides as CoFeB/MgO we need a PVD tool with a good precision for thickness deposition (~20 A for CoFeB and 10A for MgO) but also for interface roughness since in this films the anisotropy is an interface effect related mostly on the hybridization of the FeCo d orbitals and O p orbitals. For L10 ordered alloys as FePt in addition of the deposition precision of films as thin as 1-2A we need a good vacuum and low depositon rates (<0.5 A/s). On both materials we can play with the annealing in order to help the FeCo-O bond formation in MM/Ox materials and the Fe diffusion for the L10 ordered alloys of FePt. Also the Fe content can change the anisotropy properties for FeCo-O bonds and the ordering parameter on the FePt L10 ordered alloys. Results on this materials development and improvement in perpendicular MTJ structures will be presented during the talk.

But even if the stability problem seems to be solved by improving PVD tools for film process and choosing the right materials for the perpendicular MTJ stack other questions can arise in order to have an industrial device and are related to the scalability. The scalability can be limited by materials but also by nanofabrication techniques. In order to have a competing product we need to have memory pillars of 30nm or less in the size of a transistor in our days. So Applied Materials is investing a lot in development of the tools for etching in order to pattern nonmetric devices. Some results will be shared during my presentation on electrical properties of patterned MTJ using the new developed etch tools by Applied Materials.

STT-pMRAM will be able to compete with FLASH memories and SRAM if these technical aspects are solved at similar production cost. Otherwise MRAM will be used in special markets like Battery-Backed SRAM replacement and would be attractive in applications where speed and permanent data storage are needed, eliminating the use of combined memories. Some examples of applications are the replacement of components of server systems, networking and data-storage devices, home-security systems and computer printers. The consequences are enormous considering the circuit size reduction, low system energy resulting in increased battery life, enhanced performance by improving efficiency of data transfer (the computer start speed). Even more, with MTJ it will be possible to take advantage of processional dynamics for low power operation or to obtain tunable radiofrequency oscillators leading to new RF devices for the mobile phone industry.

The engineering of pMTJ for MRAM applications is a real challenge and a difficult task because good TMR and PMA properties will impose constraints and limit the working window of the device. As observed the key for improvement of device properties are the materials combination and fabrication by good mastering of the thin film growth with very precise and stable tools but also the understanding the materials properties and physical phenomenon.

[AMAT] http://insideapplied/Pages/2014_04_Endura_Anniversary.aspx

[Bai_88] M.N. Baibich, J.-M. Broto, A. Fert, F. Nguyen Van Dau, F. Petroff, P. Etienne, G. Creuzet, A. Friederich and J. Chazelas, *Giant magnetoresistance of (001)Fe/(001)Cr magnetic superlattices,* **Phys. Rev. Lett. 61** (1988) 2472.

[Ber_96] L. Berger, *Emission of spin waves by a magnetic multilayer traversed by a current,* **Phys. Rev. B 54** (1996) 9353.

[Bin_89] G. Binasch, P. Grünberg, F. Saurenbach and W. Zinn, *Enhanced magnetoresistance in layered magnetic structures with antiferromagnetic interlayer exchange*, **Phys. Rev. B 39** (1989) 4828 (R).

[Car_08] B. Carvello, C. Ducruet, B. Rodmacq, S. Auffret, E. Gautier, G. Gaudin and B. Dieny, *Sizable room-temperature magnetoresistance in cobalt based magnetic tunnel junctions with out-of-plane anisotropy,* **Appl. Phys. Lett. 92** (2008) 102508.

[Die_91] B. Dieny, V.S. Speriosu, B.A. Gurney, S.S.P. Parkin, D.R. Wilhoit, K.P. Roche, S. Metin, D.T. Peterson and S. Nadimi, *Spin-valve effect in soft ferromagnetic sandwiches*, **J. Magn. Magn. Mat. 93** (1991) 101.

[Eve_06] http://everspin.com/press.php?ppo=2006&qtype=press

[Gra_68] U. Gradmann and J. Müller, *Flat ferromagnetic epitaxial 48Ni/52Fe(111) films of few atomic layers*, **Phys. Stat. Sol. 27** (1968) 313.

[Her_10] J. Alvarez-Hérault, PhD Thesis, Grenoble University (2010).

[Hum_04] R.E. Hummel, *Understanding Materials Science - History, Properties, Applications*, 2nd Edition, Springer-Verlag, New York, (2004).

[Kat_00] J.A. Katine, F.J. Albert, R.A. Buhrman, E.B. Myers and D.C. Ralph, *Current-driven magnetization reversal and spin-wave excitations in Co/Cu/Co pillars,* **Phys. Rev. Lett. 84** (2000) 3149.

[Man_06] S. Mangin, D. Ravelosona, J.A. Katine, M.J. Carey, B.D. Terris and E.E. Fullerton, *Current-induced magnetization reversal in nanopillars with perpendicular anisotropy,* **Nature Mater. 5** (2006) 210.

[Mon_02] S. Monso, B. Rodmacq, S. Auffret, G. Casali, F. Fettar, B. Gilles, B. Dieny and P. Boyer, *Crossover from in-plane to perpendicular anisotropy in Pt/CoFe/AlO_x sandwiches as a function of Al oxidation: A very accurate control of the oxidation of tunnel barriers,* **Appl. Phys. Lett. 80** (2002) 4157.

[Moo_95] J.S. Moodera, L.R Kinder, T.M. Wong and R. Meservey, *Large magnetoresistance at room temperature in ferromagnetic thin film tunnel junctions*, **Phys. Rev. Lett. 74** (1995) 3273.

[Mor_06] A. Morisako and X.X. Liu, *Sm-Co and Nd-Fe-B thin films with perpendicular anisotropy for high-density magnetic recording media,* **J. Magn. Magn. Mater. 304** (2006) 46.

[Nak_08] M. Nakayama, T. Kai, N. Shimomura, M. Amano, E. Kitagawa, T. Nagase, M. Yoshikawa, T. Kishi, S. Ikegawa and H. Yoda., Spin transfer switching in TbCoFe/CoFeB/MgO/CoFeB/TbCoFe magnetic tunnel junctions with perpendicular magnetic anisotropy, J. Appl. Phys. 103 (2008) 07A710.

[Noz_06] J.-P. Nozières, B. Dieny, O. Redon, R.C. Sousa and I.L. Prejbeanu, Magnetic memory with a magnetic tunnel junction written in a thermally assisted manner, and method for writing the same, US Patent 7,411,817 (2006).

[Oun_02] K. Ounadjela, B. Dieny and O. Redon, High density MRAM using thermal writing, US Patent 20020281603 (2002).

[Par_91] S.S.P. Parkin, Systematic variation of the strength and oscillation period of indirect magnetic exchange coupling through the 3d, 4d, and 5d transition metals, Phys. Rev. Lett. 67 (1991) 3598. 8

[Pre_04] I.L. Prejbeanu, W. Kula, K. Ounadjela, R.C. Sousa, O. Redon, B. Dieny and J.-P. Nozières, Thermally assisted switching in exchange-biased storage layer magnetic tunnel junctions, IEEE Trans. Magn. 40 (2004) 2625.

[Puf_03] M.R. Pufall, W.H. Rippard and T.J. Silva, Materials dependence of the spin-momentum transfer efficiency and critical current in ferromagnetic metal/Cu multilayers, Appl. Phys. Lett. 83 (2003) 323.

[Rod_03] B. Rodmacq, S. Auffret, B. Dieny, S. Monso and P. Boyer, Crossovers from in-plane to perpendicular anisotropy in magnetic tunnel junctions as a function of the barrier degree of oxidation, J. Appl. Phys. 93 (2003) 7513.

[Slo_96] J.C. Slonczewski, Current-driven excitation of magnetic multilayers, J. Magn. Magn. Mater. 159 (1996) L1.

[Sun_02] J.Z. Sun, D.J. Monsma, D.W. Abraham, M.J. Rooks and R.H. Koch, Batch-fabricated spin-injection magnetic switches, Appl. Phys. Lett. 81 (2002) 2202.

[Yoo_05] I. Yoo, D.K. Kim and Y.K. Kim, Switching characteristics of submicrometer magnetic tunnel junction devices with perpendicular anisotropy, J. Appl. Phys. 97 (2005) 10C919.