Title	Palladium activated self-assembled monolayer for magnetics on silicon applications
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Publication date	2015-12-29
Original citation	Anthony, R., Ó Mathúna, C. and Rohan, J. F. (2015) 'Palladium Activated Self-Assembled Monolayer for Magnetics on Silicon Applications', Physics Procedia, 75, pp. 1207-1213. doi: 10.1016/j.phpro.2015.12.122
Type of publication	Article (peer-reviewed)
Link to publisher's version	http://www.sciencedirect.com/science/article/pii/S1875389215017617 http://dx.doi.org/10.1016/j.phpro.2015.12.122 Access to the full text of the published version may require a subscription.
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Item downloaded from	http://hdl.handle.net/10468/7591

Physics Procedia

Volume 75, 2015, Pages 1207–1213

20th International Conference on Magnetism

Palladium Activated Self-Assembled Monolayer for Magnetics on Silicon Applications

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Abstract

Magnetic thin films such as Permalloy (Py) have been extensively used as core material in integrated power magnetic components (micro-inductors and transformers) for their excellent soft magnetic properties. Existing core electrodeposition technology requires sputtered permalloy seed layer. This seed layer etches slowly compared to the electroplated core during magnetic core patterning. In this work, a new electroless deposition process has been developed where samples are activated by palladium to realize a thin catalytic layer on SiO_2. Up to 1 µm thick permalloy (~22% ±3% Fe and ~78%±3% Ni) is deposited from an in-house developed borane based bath to achieve ~ 30-35 µOhm-cm resistivities. The magnetic properties of permalloy deposits reveal distinct hysteresis loop with coercivity (~ 4.5 Oe). The electroless permalloy over-etch (12 µm) compared with sputtered permalloy seed is found to be negligible (2 µm). This demonstrates the applicability of permalloy electroless deposition as a seed for high yield batch fabrication of magnetics on silicon devices.

Keywords: Electroless deposition, Integrated inductors, Magnetics on Silicon, Over-etch, Self-assembled monolayers.

1 Introduction

An increase in converter switching frequencies is enabling inductor fabrication on silicon in CMOS-MEMS compatible processes with footprints as small as 2 mm^2. To enhance the inductance significantly a thin magnetic material, which acts as a core, is deposited to confine the flux generated from current carrying Cu windings. Ni-Fe based alloys still remain the most widely used core magnetic materials. Previous reports have described Ni-Fe alloy processing via electroplating [Park et. al. (2003), Brandon et. al. (2003), Flynn et. al. (2006)] and sputtering [Mullenix et. al. (2013)]. But electrodeposition is an economically viable process for thick deposits with excellent film characteristics. The electroplating process requires a thin electrically conductive seed layer which is vacuum deposited prior to

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Selection and peer-review under responsibility of the Scientific Programme Committee of ICM 2015

doi:10.1016/j.phpro.2015.12.122

electrodeposition. In a subsequent fabrication step the seed layer and the electroplated core are wet etched through a photoresist mask to realize patterned geometries. This step can result in decreased yields. The problem becomes a major roadblock when the device footprint needs to be reduced. The etchant readily removes the electroplated core while the sputtered seed is etched at a significantly lower rate resulting in a horizontal over-etch as depicted in figure-1 (b). This can be attributed to the sputtered seed which has high density structure due high energy bombardment of ions deposition. While electroplating process is low energy process, the films are less dense in nature. To compensate this the dimension of the core is oversized in the mask layout resulting in 'core feet' on the substrate surface shown in figure-2. However, the additional core material contributes to eddy current losses decreasing the inductance at low frequencies and increasing the overall device footprint [Wang et. al. (2007)]. Hence, it is apparent that new processes to curtail over-etch would be highly advantageous. The authors [Anthony et. al. (2014), Anthony et. al. (2014)] have previously reported thick resist process to reduce over-etch, however no complete solution to wet-etch over-etch has been reported to date.

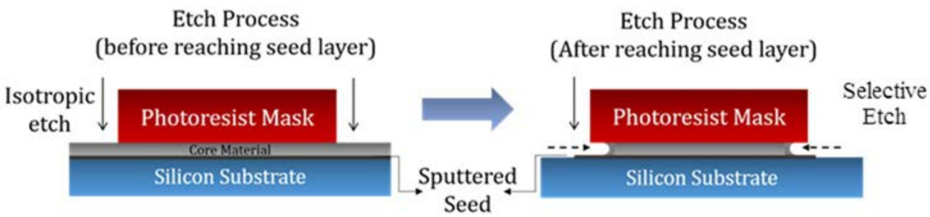

Fig. 1. (a) Isotropic etch process before reaching seed layer. (b) Selective etch behaviour after reaching seed layer.

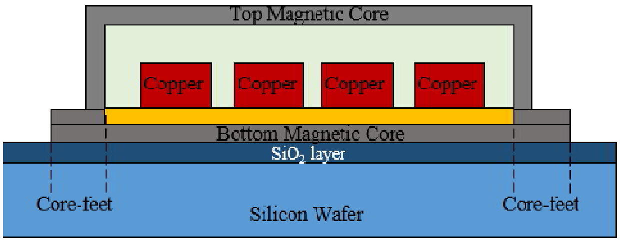

Fig. 2. Schematic of a racetrack inductor with core-feet highlighted.

In this work a new process has been employed to deposit permalloy to eliminate core over-etch. A detailed activation process with palladium to form a thin conductive layer on an SiO_2 surface is described followed by an in-house electroless permalloy deposition process. The adhesion of the deposited films is tested by standard scotch tape and pull-tester unit. The magnetic properties of the deposited film is measured in static mode. Finally, etch comparisons between the electroless permalloy films and sputtered permalloy are made.

2 Experimental Details

To understand the influence of the seed layer in the wet etching procedure, two different samples were prepared. Silicon wafers <100> were cleaned and oxidized to achieve a thin SiO_2. The samples were pre-cleaned in acetone, iso-propyl alcohol (IPA) and DI water. This was followed by plasma treatment in a March Plasmod, GCM-200, system in an oxygen atmosphere at 100 W for 5 mins. The samples were immersed in (3-Aminopropyl)triethoxysilane (APTES) solution for 30 mins. The APTES molecules form bonds with the sample surface leading to a thin adhesive self-assembled monolayer shown in figure 3. The excess SAM is removed from the surface of the substrate by sonication resulting in a SAM. At this stage, the samples are heated at 65ºC in an in-house prepared palladium solution to form a thin catalytic layer. Figure 3 depicts the formation of thin Pd^{2+} on the sample substrate through the amine bonds. It is important to note that SAMs adhere to the thin naturally oxidized layer on silicon. The palladium acts as nucleation centers for subsequent electroless metal deposition.

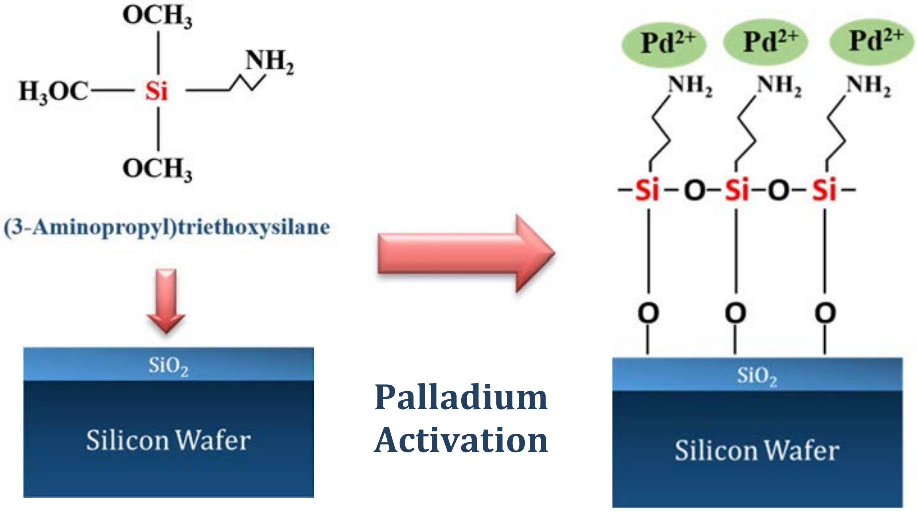

Fig. 3. Schematics of self-assembled monolayer deposition process and Pd^{2+} deposition as catalyst layer.

At this stage the sample is ready for permalloy deposition. The samples were cleaned in DI and purged with nitrogen gas. An in-house borane based bath developed for electroless permalloy deposition has been described earlier [8]. This bath composition has been optimized to achieve uniform film on Cu. Permalloy films are electrolessly deposited using bath conditions (pH~ 6.5 and temperature~ 75 ºC. The deposit thicknesses are recorded versus time using a surface profilometer (Tencor Alpha-step 200). Thicknesses up to ~1 μm could be obtained in 900 seconds of deposition. It is important to note that Fe can be preferentially deposited by altering the DMAB content of the bath [Anthony et. al. (2015)].

3 Results and Discussions

Figure 4 illustrates the deposition thickness of the film achieved with immersion time. The deposition rate increases as the bulk conductivity of the deposit increases and eventually the rate tends to saturate. It is important to note that thickness ~ 1 μm could be achieved with the deposition process. Thicker deposits (> 1 μm) have shown high stress, poor adhesion and in some cases delamination of the films. Scanning electron microscope (SEM) images of the permalloy deposits with and without oxygen plasma treatment were obtained. As shown in figure 5(a-b), the deposits without oxygen plasma exhibited fractal growth. This growth mechanism is attributed to directional growth preference due to local inequilibria [Sander et. al. (1986)]. Deposits with 15 minutes oxygen plasma preclean led to smooth growth (figure 5 (c)). This can be attributed to the surface oxidation which improves hydrophilicity of the SiO_2 substrate for further oxygen/silicon bonds from the APTES molecule. The amine groups are then available for Pd^{2+} ion interaction which forms the activation layer for subsequent electroless magnetic material deposition. This process could be significant interest for depositing metals on dielectric surfaces for MEMS applications [Anthony et. al. (2015)].

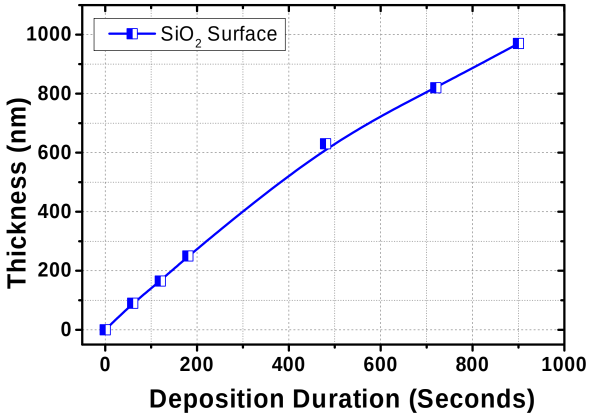

Fig. 4. Deposition rate of permalloy deposits on SiO_2surface.

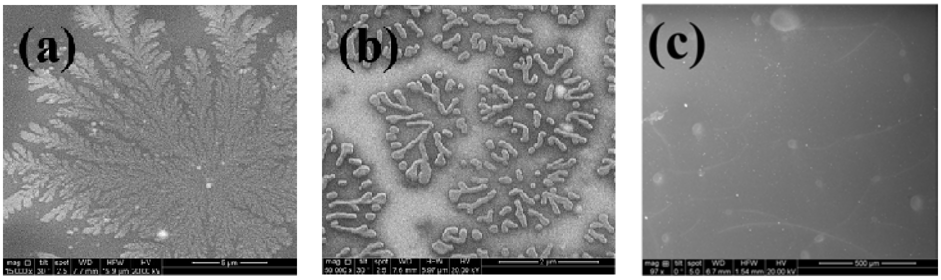

Fig. 5. SEM micrograph of: (a-b) Fractal permalloy growth observed on Si surface without oxygen plasma treatment and (c) Smooth permalloy deposition after plasma treatment.

The energy dispersive x-rays (EDX) analyses were performed at different stages of magnetic seed deposition process. Figure 6(a) shows the micrograph of a palladium EDX spectrum. It confirms the presence of palladium prior to permalloy deposition. This is followed by electrolessly depositing permalloy. Figure 6(c) depicts the EDX results of the sample which exhibited distinct Ni and Fe peaks with suggested Ni (78%±3%) and Fe (22%±3%) composition. It is important to note that the nature of nucleation and layer growth plays a critical role in determining the magnetic properties. The resistivities of the films were found to be 30-35 µOhm-cm, higher than PVD/electroplated permalloy films (20 µOhm-cm). This can be assumed that a small % of boron being co-deposited with the film. Light element like boron with low photon energies cannot be detected in the EDX spectrum [Ruiz-Vargas et. al. (2014)].

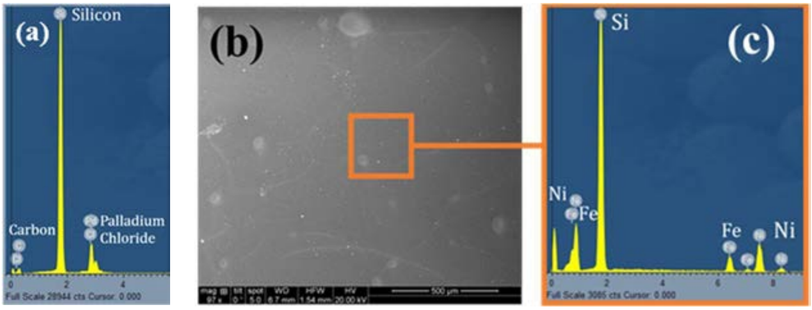

Fig. 6. (a) EDX spectrum of Pd catalyst on Silicon surface and (b) SEM micrograph after electroless permalloy deposited on palladium catalyst with corresponding EDX spectrum (c).

The deposits were tested in a BH loop tracer (SHB instruments, Model: MESA 200 HF) up to 250 Oe external magnetic field. A coercivity of ~ 4.5 Oe and saturation flux density of ~ 0.95 T was obtained from the BH loop tracer. However, it should be noted that deposition conditions and bath composition can change the Ni-Fe composition [Anthony et. al. (2015)]. This is critical in determining the coercivity, saturation flux density (B_{Sat}) and resistivity of the films. Figure 7 depicts the hysteresis loop of ~ 100 nm thin permalloy film electrolessly deposited on palladium activated SAM layer.

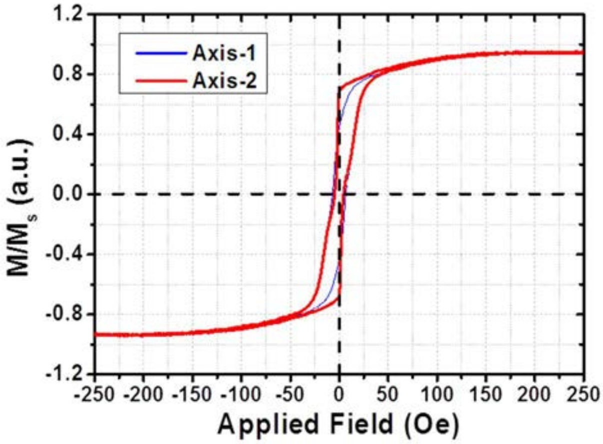

Fig. 7. Hysteresis curve of 100 nm permalloy deposit.

Two 100 nm thick permalloy samples (sputtered and electrolessly deposited) were prepared and deposited with 2 μm $Ni_{45}Fe_{55}$. It is then patterned with ~ 9 μm AZ 9260 on a Cannon PLA-501 FA (g-h-i) mask aligner. Diluted HNO_3 etchant was prepared with 1:2 DI water and cooled down to room temperature. The accessible core material were etched in it in puddle mode to remove permalloy (electroless and sputtered) completely from the patterned regions. As observed from microscopic images in figure 8, some seed material may still remain between the cores, thereby resulting in core shorting, so etching is continued. Nearly ~ 2 μm undercuts were observed compared to 12 μm-15 μm in the sputtered seed layer samples to completely remove uncovered core material.

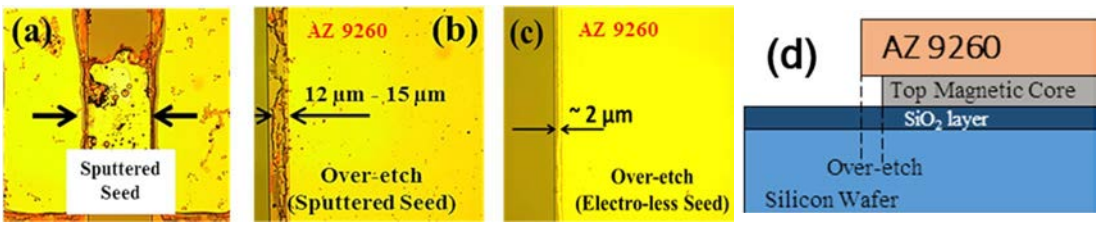

Fig. 8. (a) Sputtered seed remaining while etching in some regions. (b) Over-etch with sputtered and (c) electroless permalloy. (d) Schematic illustration depicting magnetic core over-etch.

4 Conclusion

In conclusion, we have presented a new magnetic thin film (~ 1 μm) deposition process on silicon by activating the surface as seed layer for integrated magnetic components. Static magnetic characteristics suggest coercivity ~ 4.5 Oe with resistivity 30-35 μOhm-cm. The electroless magnetic film patterned with commercially available AZ9260 photoresist was compared with a sputtered seed of similar thickness (~ 100 nm). Over-etch for the electroless plated permalloy is only 16.67 % of that achieved with the sputtered permalloy film. Moreover, this new deposition technique could eliminate the need for additional core-feet which reduce would device footprint and reduce core losses and could be employed to replace conventionally deposited sputtered seed for metal plating in MEMS processing.

5 Acknowledgement

The authors wish to acknowledge Central Fabrication Facilities (CFF) at Tyndall National Institute for the support and European Union for funding the work through FP7 (Project: PowerSwipe) under grant no.: 318529. The authors would also like to acknowledge Dr. Santosh Kulkarni for useful discussions on the work.

References

Park, J. W., Allen, M. G. (2003) Ultralow-profile micromachined power inductors with highly laminated Ni/Fe core: Application to low-megahertz DC-DC converters, IEEE T. Magn., vol. 39, no. 5, pp. 3184-3186.

Brandon, E. J., Wesseling, E., White, V., Ramsey, C., Castillo, L. D., Lieneweg, U. (2003) Fabrication and characterization of microinductors for distributed power converters, IEEE T. Magn., Vol. 39, No. 4, pp.2049-2056.

Flynn, D., Sudan, N. S., Toon, A., Desmulliez, M. P. Y. (2006) Fabrication process of a micro-inductor utilizing a magnetic thin film core, Microsys. Technol., Vol. 12, Iss. 10-11, pp. 923-933.

Mullenix, J., El-Ghazaly, A., Wang, S. X. (2013) Integrated transformers with sputtered laminated magnetic core, IEEE T. Magn., vol. 49, No. 7, pp.4021-4027.

Wang, N., O' Donnell, T., Roy, S., McCloskey, P., O' Math'una, C. (2007) Micro-Inductors integrated on silicon for power supply on a chip, J. Magn. Magn. Mat., vol. 316, e233-237.

Anthony, R., Wang, N., Kulkarni, S., O' Math'una, C. (2014) Advances in planar coil processing for improved micro-inductor performance, IEEE T. Magn., vol.50, Iss. 11, 8401804.

Anthony, R., Kulkarni, S., Wang, N., O' Math'una, C. (2014) Advanced Processing for High Efficiency Inductors for 2.5D/3D Power Supply in Package, IEEE International Conference on 3D System Integration (3DIC), pp 1-4, Kinsale, Ireland.

Anthony, R., Shanahan, B., Waldron, F., O' Math'una, C., Rohan, J. F. (2015)Anisotropic Ni-Fe-B films with varying alloy composition for integrated magnetics on silicon applications, Appl. Suf. Sci., vol. 357, pp. 385-390.

Sander, L. M. (1986) Fractal growth processes, Nature, vol. 322, Iss.28, pp.789-793.`

Anthony, R., O' Math'una, C., Rohan, J. F. (2015) Electrochemical process for fabrication of laminated micro-inductors on silicon, 41st Micro and Nano Engineering Conference (MNE), The Hague, Netherlands.

Ruiz-Vargas, J., Siredey-Schwaller, N., Noyrez, P., Mathieu, S., Bocher, P., Gey, N. (2014) Potential and limitations of microanalysis SEM techniques to characterize borides in brazed Ni-based superalloys, Mater. Charact., vol. 94, pp.46-57.