Uniform nanoparticle based monolayers deposited by a modified spin coating technique

K. Subramanya Mayya, In-Seok Yeo, U-In Chung, and Joo Tae Moon

Process Development Team, Memory Division, Samsung Electronics Co. Ltd.
San#24 Nongseo-Ri, Giheung-Eup, Yongin-Si, Gyeonggi-Do, Korea 449-711
mayya@samsung.com

ABSTRACT

Controlled deposition of uniform cobalt nanoparticle based monolayers by a modified spin coating procedure wherein, the uniformity is demonstrated over the macroscopic scales is described. The nanoparticle dispersion rested on the entire area of the 6 inch silicon wafer for a curing time of 5 min after which the substrate was spun at 6000 rpm. The substrates were pre-coated with an alkyl terminated self assembled monolayer to assist the formation of nanoparticle based monolayer. A time dependent adsorption of nanoparticles was observed wherein the surface coverage of nanoparticles increased with curing time. The method described here is general and offers new opportunities to successfully employ the deposited films for nanoparticle based devices and related applications.

Keywords: Nanoparticles, self-assembly, spin coating, cobalt nanoparticles, self-assembled monolayer.

INTRODUCTION

Interest in metal and semiconductor nanoparticles stems mainly from their size dependent properties that are the basis of a number of novel devices that have been reported so far.[1] Among the various methods available for their synthesis, solution based wet chemical methods based on the "bottom-up" approach offer better control over their size, shape and composition.[1,2] In order to harness the interesting properties of this intermediate state of matter for device applications, it is necessary to immobilize them on suitable surfaces/substrates. Till date a number of strategies have been developed for this purpose that include, electrostatic layer-by-layer self assembly,[3] Langmuir-Blodgettry,[4] oligonucleotide directed assembly,[5] organization driven by controlled evaporation of solvent, etc.[6] While these strategies allow formation of uniform films on a limited area of the substrate, they are not easily scalable due to various limitations inherent in these strategies. Therefore, new strategies preferably using preexisting techniques that are widely used in the industry need to be developed in order to exploit the interesting size dependent properties of the nanoparticles for various applications.

Spin coating technique is widely used in the industry to controllably deposit solution based materials like photoresists, polymers etc. Recently, nanoparticle based films have has also been deposited using this procedure. Hong *et al* reported on the deposition of cobalt and silver nanoparticles by spin coating.[7] They observed that nanoparticles based films can be successfully deposited provided that the depositing solution wets the underlying substrate. Also, the surface coverage of nanoparticles increases with increasing particle concentration in the depositing solution. However, multilayer formation was observed at sub-monolayer surface coverage beyond a certain particle density. Kodama *et al* reported deposition of uniform FePt nanoparticle based films with uniformity demonstrated over 2.5 in. silicon disk.[8] Their technique involved controlled evaporation of solvent by controlling the vapor pressure inside the deposition chamber whilst spin coating; however, deposition of nanoparticle based films below 3 monolayers was not demonstrated. As discussed above, while deposition of multilayer and sub monolayer films are reported, few reports exist on the deposition of close packed monolayer films with uniformity demonstrated over macroscopic scales.

Here we report a simple procedure for the deposition of uniform cobalt nanoparticle based monolayers with uniformity demonstrated over a *6 inch diameter, silicon wafer* by a modified spin coating process. The nanoparticles were deposited from the organic solvents, while the substrate was pre-coated with a self assembled monolayer in order to suitably wet the nanoparticles/depositing solution. Deposition characteristics were dependent on the adsorption time (curing time), particle concentration and the spinning speed. Our method involves a modified spin coating procedure wherein the depositing solution rested on the entire area of the substrate during the period of the curing time.

EXPERIMENTAL

Cobalt nanoparticles of sizes 6-8 nm were synthesized using the modified "polyol process" wherein 1,2 dodecanediol is used as the reducing agent.[9] A typical synthesis involved heating to 200°C a mixture of Cobalt (II)acetate tetrahydrate (1 g) and oleic acid (1.3 mL) in 40 mL octyl ether. When the reaction mixture reaches 200°C, 1.5 mL of trioctylphosphine was added. The solution

temperature was ramped to 240°C and allowed to stay at this temperature for 10 min. The solution was then cooled to room temperature followed by addition of absolute ethanol in order to separate the particles. The particles were separated by centrifugation at 5000 rpm for 5 min., and subjected to additional 2 washing steps. The obtained particles were redispersed in 10 mL toluene containing 50μL of Oleic acid and used as stock solution. The particles were characterized using transmission electron microscopy (Figure 1).

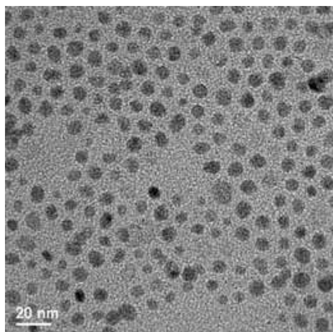

Figure 1: Transmission electron microscopy image of cobalt nanoparticles synthesized using the polyol process.

Surface modification of the silicon oxide was rendered by adsorption of Octadecyltrichlorosilane (OTS) from a 1mM solution of OTS in toluene for 15 min. Silicon wafer with 100 nm thermal oxide were pre-cleaned by sonication in isopropyl alcohol, and water followed by heating in a solution containing hydrogen peroxide, ammonia solution and water in the ratio 1:1:5 at 70°C for 10 min. The substrates were then cleaned with copious amounts of water. Nanoparticle based film was deposited by mounting the OTS modified wafer on the spin coater followed by spreading the cobalt colloid solution evenly on the wafer and allowed to stay for some time (will be referred to as *curing time*). The deposition process concluded with spinning the substrate at required speed (3000 ~ 6000 rpm) for 30 sec. Toluene (boiling point = 110°C) was chosen over other solvents since, our procedure involved a curing time at room temperature during which the evaporation of toluene is relatively slow, thus maintaining a constant concentration through period of the curing time.

DISCUSSION

Literature reports suggest that substrate wetting of the depositing solution is necessary to obtain uniform deposition using spin coating.[7,8] Furthermore, typical nanoparticle synthesis involves addition of stabilizing agents in the stock solution to prevent aggregation. These stabilizing agents (in this example oleic acid) affect the wetting behavior of the adsorbing/depositing solution. In our case, even though toluene wets the oxide surface, nanoparticles did not deposit on to the unmodified substrate with or without the curing step. Therefore, substrates were modified by depositing a self assembled monolayer of OTS to improve the interaction of nanoparticles with substrate via OTS. On surface modification, toluene based depositing solution exposed even higher contact angle but allowed the formation of nanoparticle based films.

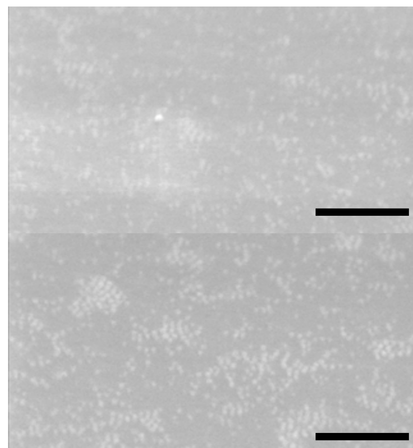

Figure 2: Scanning electron microscopy image of Co nanoparticles deposited onto OTS modified silicon wafers at curing times 0(A) and 100 sec (B). Scale bar = 180 nm.

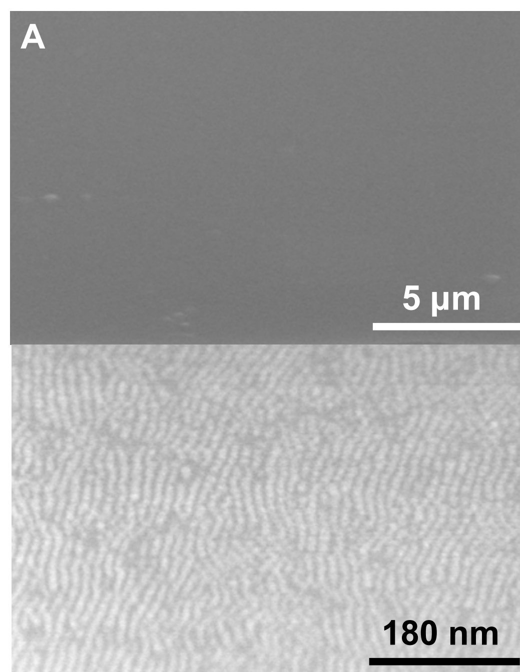

Figure 3: SEM images of Co nanoparticles deposited onto OTS modified silicon substrates at 5 min curing time.

NSTI-Nanotech 2005, www.nsti.org, ISBN 0-9767985-0-6 Vol. 1, 2005

Our deposition method is a modification of the conventional spin coating procedure wherein the depositing solution rested on the entire area of the substrate for 5 minutes. During this period nanoparticles adsorbed onto the OTS modified substrate.

A time dependent adsorption study showed that the surface coverage of nanoparticles increased with curing time. Figure 2 shows SEM images for films deposited using curing time 0 (figure 2A) and 100 sec (Figure 2B).. The particle density increased from 1.3×10^{11} to 2.6×10^{11} per cm^2 with a curing time increment of 100 sec clearly indicating the curing time dependent increase of nanoparticle density. A low degree of local ordering among the deposited nanoparticles can also be observed in the sample deposited at 100 sec curing time (Figure 2B). At 5 min curing time, scanning electron microscopy analysis (Figure 3B) showed that nanoparticles formed close packed monolayer with relatively high degree of ordering. As can be seen from figure 3, the nanoparticle based monolayer obtained is uniform on the macroscopic scale (Figure 3A) with uniform separation at the nanoscale (Figure 3B). The particle density was calculated to be 0.96×10^{12} particles per cm^2 which is higher than previously reported for nanoparticle based monolayer films deposited using spin coating. The most likely reason for the ordering (not observed in the previous reports) is due to the combined effect of attractive non-covalent particle-particle and particle-substrate interactions assisted by forces involved in the spin coating. Our depositing solution contained added surfactants with high boiling points which might also play an important role in the ordering. Formation of ordered superlattice structures in the presence of excess capping agents was previously observed by Klabunde *et al*.[10] Future work would involve the study on the effect of various solvent and concentration dependent study on the presence of various surfactants. This method of deposition was successfully extended to other nanoparticles systems with smaller sizes (data not included). Preliminary results suggest that, the principle behind the deposition scheme described here could also be used to realize monolayer films using dip coating. Further work on this is currently underway.

SUMMARY

To conclude, macroscopically uniform nanoparticle based monolayer films with relatively high degree of nanoscale order has been deposited using a modified spin coating procedure. The method described here is highly reproducible and the uniformity was successfully demonstrated over a 6 inch silicon wafer. The substrates were modified using a self assembled monolayer of organosilane *that assisted* the formation of monolayer films of preformed cobalt nanoparticles. The process involved a curing time during which the nanoparticle sol rested on the entire area of the substrate. The deposited films show great promise for their use as charge storing element in the nanoflash memories. An important advantage of this method is the thin monolayer films are deposited using the already established coating methods in the fabrication line.

REFERENCES

1. (a) S. Sun, C. B. Murray, D. Weller, L. Folks, A. Moser, *Science*, **287**, 1989 (2001). (b) X. G. Peng, L. Manna, W. D. Yang, J. Wickham, E. Scher, A. Kadavanich, A. P. Alivisatos, Nature, 404, 59 (2000).
2. (a) D. L. Feldheim, C. A. Foss, *Metal Nanoparticles: synthesis, characterization and applications*, Marcel Dekker N.Y. (2002). (b) L. Manna, D. J. Milliron, A. Meisel, E. C. Scher, A. P. Alivisatos, Nature Materials, 2, 382 (2003).
3. G. Decher, Science, 277, 1232 (1997).
4. M. Sastry, M. Rao, K. N. Ganesh, Acc. Chem. Res. 35, 847 (2002).
5. J. J. Storhoff, C. A. Mirkin, Chem. Rev. 99, 1849 (1999).
6. (a) C. M. Niemeyer, Angew. Chem. Int. Ed. 40, 4128 (2001). (b) I. Willner, E. Katz, A. Shipway, Chem. Phys. Chem. 1, 18 (2000) and references therein.
7. Y.K.Hong, H.Kim, G. Lee, W. Kim, J.I.Park, J. Cheon, J. Y. Koo, Appl. Phys. Lett. 80, 844 (2002).
8. H. Kodama, S.Momose, N. Ihara, T.Uzumaki, A. Tanaka, Appl. Phys. Lett. 83, 5253, (2003).
9. C.B.Murray, S. Sun, W. Gaschler, H.Doyle, T.A.Betley, C.R.Kagan, IBM J. Res. & Dev. 45, 47 (2001),.
10. X. M. Lin, H. M. Jaeger, C. M. Sorensen, K. J. Klabunde, J. Phys. Chem. B. 105, 3353 (2001).