Growth of ferromagnetic core-shell Fe-Sm-Ta-N nanosperoids.

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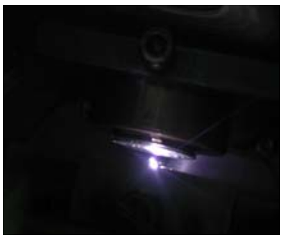
Abstract

Sm-Fe-Ta-N core-shell (CS) nanospheroids were fabricated from hot liquefied nanodroplets by 157 nm pulse laser deposition in nitrogen gas. The $Sm_{13.8}Fe_{82.2}Ta_{4.0}$ intermetallic alloy was used as the target. At low laser energy (20 mJ), spherical CS of 1-35 nm radius were fabricated on a Si/Ta substrate forming uniform films. The small nanodroplets were grown in the plume from the gas phase, and the larger ones (>50 nm radius) from the target's hydrodynamic ejection. The critical radius of the droplets and their surface energy per unit area was found to be 7.5 nm and 3.8 μJ/cm² respectively. A number of CS solidified in the plume and consist of 2.5-5 nm radius crystalline nucleus surrounded by a <35 nm radius amorphous spherical shell. This structure prevents the oxidization of the crystalline nucleus because oxidization is confined on the surface of the CS. Furthermore, multi-crystalline nanodomains (embryos) were identified in a single CS from both homogeneous and heterogeneous nucleation.

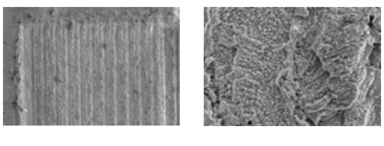
Experimental set-up

The mechanism that leads to material ablation depends on:

- Laser characteristics
- Properties of the target
- Properties of the substrate
- Distance between the target and the substrate and geometry,
- Background gas (type and pressure)



- F_2 Laser: 157nm, E =1-50mJ/pulse, 15-20 Hz repetition rate
- Target : $Sm_{13.7}Fe_{86.3}$, $Sm1_{3.8}$ $Fe_{82.2}Ta_{4.0}$
- Substrate : Si / Ta
- Distance between target and substrate 0.2-1.5 cm
- Different directions of the substrate: 90°, 180°, 270°.
- Background gas: N_2 101 KPa (1 atm)



SEM images of the etched Sm-Fe-Ta target after ablation. a) The lines were 100μm wide, b) higher magnification of previous figure. The image shows high temperature gradients during target's irradiation.

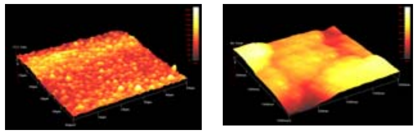
Results and Discussions

AFM analysis of SiTa substrate surface

Substrate: Si

Sputtered Ta: Sputtering apparatus CemeCon CC800/7 (working pressure 1-2·10⁻³mbar)

Results: 100 nm Ta film

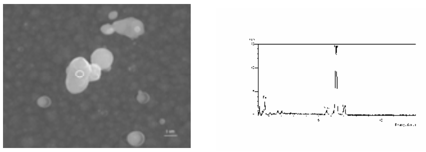


SEM/EDX analysis

Substrate: Si + 100 nm Ta

Background pressure: high vacuum (10^{-6}mbar)

Results: Amorphous film, with droplets of ablated material (X-ray analysis on a droplet)



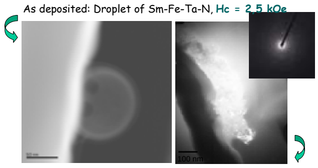
Experimental +TEM examination

Conditions:

Substrate: Si + 100 nm Ta. Target: $Sm_{13.8}Fe_{82,2}Ta_{4,0}$

Background gas: N_2 101 kPas

As deposited: Droplet of Sm-Fe-Ta-N, **Hc = 2,5 kOe**



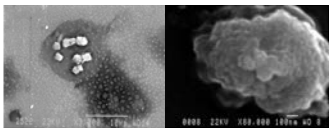
After annealing and nitriding, nanocrystalline thin layer, **Hc = 5 kOe**

Experimental +SEM examination

Conditions: E= 50 mJ

Substrate: Si + 100 nm Ta. Target: $Sm_{13.8}Fe_{82,2}Ta_{4,0}$

Background gas: N_2 101 kPas



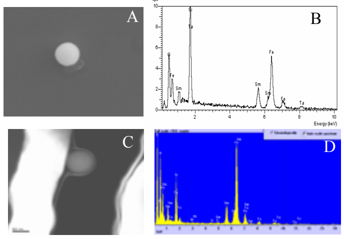
SEM images of surface morphology of films grown at 50 mJ. The hot plume condensates to form crystal agglomerations of asteroid shape.

Different direction of substrate

Conditions: E= 20 mJ

Substrate: Si + 100 nm Ta. Target: $Sm_{13.8}Fe_{82.2}Ta_{4.0}$

Background gas: N_2 101 kPas



The number of large size nanodroplets on the Si/Ta substrate in the direction opposite to the laser beam (180°), Fig. A, was by 80% higher than of the order of two directions at 90° and 270° , Fig. C. The atomic elemental concentration of droplets larger than 100 nm, reflected the concentration of the target and the average concentration of Fe, Sm and Ta was 79%, 19% and 2% respectively , Fig. B. On the contrary, the average elemental concentration of Fe, Sm and Ta of the smaller nanodroplets, Fig. *C* was 58 %, 24%, and 18%, Fig. D.

Calculation of surface energy per unit area of the liquid nanodroplet

The reduction of the free energy corresponding to sphere nucleation of radius *r*, is given by the relationship

$$\Delta G = -\tfrac{4}{3}\pi r^3 \Delta G_0 + 4\pi r^2 \sigma$$

σ: surface free energy (gas/liquid) per unit area , ΔG_o : free energy difference between the gas and liquid,

$$\Delta G_0 = -\frac{\rho RT}{M}\ln\left(\frac{c}{c_s}\right),$$

ρ : density of the droplet ~8.7 g/cm³, M :molecular weight, c : concentration of one of the elements in the droplet solution c_s is the concentration of the saturated solution.

$$\Delta G_0 = 2\frac{\sigma}{r^*}$$

The free energy attains its maximum value when the radius of the nanodroplets attains a critical value r*.

$$\Delta G_0 = \frac{16\pi\sigma^3}{3(RT\rho)^2}\frac{M^2}{\ln(S)^2}$$

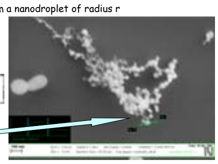
The maximum value of ΔG_0 at the critical point is called the critical free energy for nucleation and equals towhere $S = C/C_s$

$$W(r) \sim \exp\left[-\frac{\Delta G}{kT}\right]$$

The probability W(r) to form a nanodroplet of radius r

Using the above equations

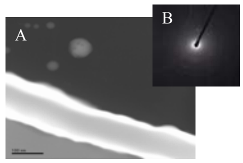
$$\ln W(r) \sim \frac{4\pi}{kT}\left[\sigma r^2 - \Delta G_0 r^3\right] = \frac{4\pi\Delta G_0}{3kT}\left[\frac{3}{2}r^* r^2 - r^3\right]$$



The critical radius r* of the nanodroplets is ~7.5 nm.

Surface energy per unit area of the liquid nanodroplet for $Sm_{13.8}Fe_{82.2}Ta_{4.0}$: 3.8 μJ/cm²

Nanodroplet's size and contact angles



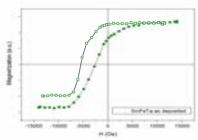
A. Typical TEM image of a single ~31 nm nanodroplet and few smaller ~9–15 nm. Inside the larger nanodroplet, four different 4 nm Sm–Fe–Ta–N cores were formed surrounded by amorphous material.
B. Diffraction pattern of nanodroplet of Fig. A where the crystal structure of the embryos is verified

TEM image of clusters of nanodroplets attached with the substrate with different contact angles.

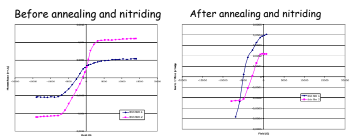
Magnetic measurements – VSM

Before annealing and nitriding: Hc= 2,5 kOe

After annealing and nitriding: Hc= 5 kOe



Magnetic measurements - VSM



Distance between target and substrate 1.5 cm
Laser energy 40 mJ, growth for 45 minutes (Sample 1)

Distance between target and substrate 0.5 cm
Laser energy 40 mJ, growth for 60 minutes (**Sample 2**)

Conclusions

- Thin uniform nanodroplet films, were deposited on Si/Ta substrates from Sm–Fe–Ta target with PLD at 157 nm at low laser energy in nitrogen.

- By analyzing the stochiometry and the morphology of a large number of nanodroplets, it was found that nanodroplets less than 100 nm were formed mainly in the plume.

- The critical radius was 7.5 nm and the surface energy per unit area was 3.8 μJ/cm². Larger nanodroplets retain the target stochiometry with small RMS deviation and therefore originate from hydrodynamic ejection from the target.

- The majority of medium size core-shell nanodroplets consist of two phases, a 2.5–5 nm crystalline nucleus surrounded by an amorphous shell. This structure minimizes nanocrystal's oxidization and is responsible of ferromagnetic response from core-shell film morphologies.