FeSi THIN FILMS DEVELOPED BY PULSED LASER DEPOSITION

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În lucrare sunt prezentate rezultate asupra unor straturi subţiri din FeSi depuse prin ablaţie laser pe subtrat de siliciu, siliciu acoperit cu platină, cuarţ, ceramică SITAL şi sticlă (tip BK7). A fost studiată influenţa parametrilor de depunere (presiunea în camera de depunere, lungimea de undă, fluenţa laser) asupra structurii şi morfologiei straturilor subţiri: structura suprafeţei şi interfaţa film-substrat, proprietăţile electrice şi magnetice au fost în mod special investigate din această perspectivă.

This paper presents some results on FeSi thin films deposited by pulsed laser deposition on silicon, platinum covered silicon, quartz, SITAL ceramic and glass (type BK7) substrates. The influence of the deposition parameters (background pressure, laser wavelength, laser fluence) on the structure and morphology of the thin films was studied: the thin film superficial and thin film-substrate interface characteristics, the electrical and magnetic properties were particularly investigated from this perspective.

Keywords: FeSi, thin film, PLD

1. Introduction

With all its remarkable properties, when used in AC magnetic devices, the industrial iron (or soft iron) has two major disadvantages: high electrical conductivity and bad magnetization loops (magnetic hysteresis; both leading to important energy losses. To reduce such losses and/or to improve the quality of electrical devices, soft iron must be used in alloys together with other elements; the most important and common of these is silicon (Si). FeSi alloys maintain their magnetic properties up to 33% Si content (expressed as mass percentage, that corresponds to 50% atomic percentage. These types of alloys are used mainly for the construction of electrical machinery, electrical transformers and in power equipment that works at the industrial AC frequency (50 or 60 Hz). Such alloys, used in different forms and composition varieties, represent the best economical combination in terms of production costs and magneto-mechanical properties.

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FeSi alloys are an important part in the evolution of the production, transport and utilization of electricity [1-3].

Silicon is soluble in the α-Fe (the bcc form) up to 15% mass (corresponding to about 25% atomic percents). The Si atoms substitute the Fe atoms without significant modifications to its crystallographic structure, except a minor reduction of the lattice constant. The most important effect is the disappearance of the γ-Fe (the fcc form), between temperatures of 900 to 1400°C and a Si content of more than 2.2%; this allows the sheets to re-crystallize at high temperatures (1000–2000°C) without reaching a critical point when cooled. Alloying Fe to Si brings several improvements to the material properties: 1.) the suppression of phase transformation between $\alpha \leftrightarrow \gamma$ Fe, allowing thermal annealing at high temperatures (usually above 900°C) that lead to internal atomic detensioning and favor re-crystallization of the material; 2.) an increase in the electrical resistivity of the material, that leads to lower losses by turbionary currents; 3.) a decrease of magnetostriction, proportional to the Si content; 4.) a decrease in the magnetocrystalline anisotropy, hence an increment in the permeability of the alloy; 5.) reduction of the magnetic ageing by blocking the interstitial atoms (such as carbon), leading to longer stability; 6.) an increment in the hardness and strength of the material, that makes it suitable for processing in different geometrical forms as sheets [1-5].

Thin films of such alloys are usually developed by deposition means such as sputtering techniques [6], molecular beam epitaxy (MBE) [7], or metal organic chemical vapor deposition (MOCVD) [8], although some papers deal with alternative non-conventional methods, such as pulsed laser deposition (PLD) [9-15]. In this paper, the alternative method of PLD was used to obtain FeSi thin films. This technique is clean and simple, and was demonstrated to be effective for the growth of films with a wide range of compositions, structures and properties [9-15]. Such films may be used in applications involving semiconductors, solar cell development and/or sensor technology [16, 17], catalysts [18], special destination electrodes [19], etc.

2. Experimental conditions

2.1. Method

PLD consists of material ablation by bombarding the surface of a target with short energetic pulses of a focalized laser beam, at a certain chosen wavelength. This process takes place in a vacuum chamber where there is a low, constant pressure, in vacuum or in a special gas (e.g. argon). Due to the high power density of the beam, a plume-shaped plasma is generated perpendicular to the target surface at the incident point (figure 1). The substrate to be coated is placed a few centimeters away from the target facing the top of the plasma plume. Detailed information on the procedure and different experimental setups is presented elsewhere [12-15].

2.2. Target and sample preparation

For the deposition experiments of FeSi thin films we used two types of targets: a cylindrical shaped (φ = 20 mm and 7 mm thick), made from FeSi powder (3% Si content, purchased from *Merck KGaA*) pressed at 10 t/cm^2, and a square target made from a transformer FeSi-steel sheet (type 310), cut as a 30 x 30 mm and 0.6 mm thick square piece (figure 2).

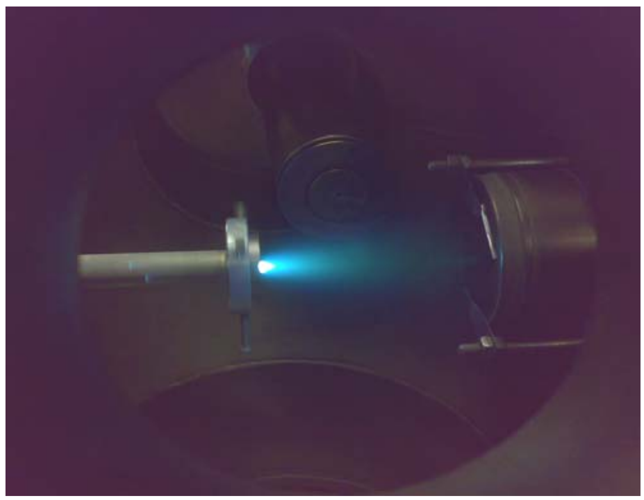
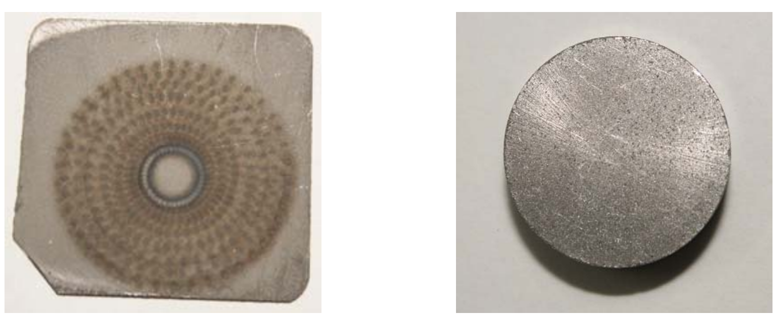


Fig. 1. An inside view of the PLD setup during FeSi thin film deposition



a.) **b.)**

Fig. 2. Photographs of the FeSi targets used for thin film deposition: a FeSi-steel sheet, 3 x 3 mm (a), and a φ = 20 mm and 7 mm thick, cylindrical shaped one

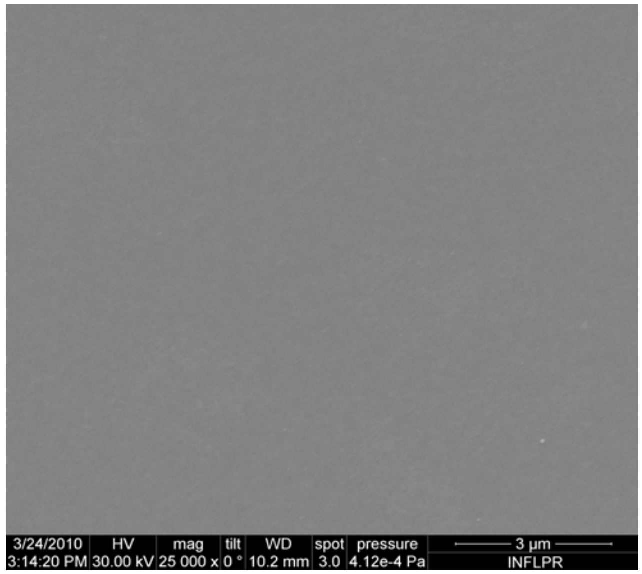
Preparation of the target for PLD is done in three steps: at first, it is hand-polished using carborundum powder (SiC 312, nanometric sized) on a cast iron rotating plate. Polishing the target using fine Al_2O_3-based powder is the second step, after which it is polished using a diamond-based powder. The substrates (silicon, platinum covered silicon, quartz, SITAL ceramic, and type BK7 glass) were firstly cleaned in an ultrasonic bath for 15 minutes, using acetone and isopropanol as cleaning mediums, then dried under nitrogen pressured gas.

The energy source we used was an Ar:F excimer laser, working at $\lambda = 193$ nm and 50 Hz; the laser spot area was 3 mm^2 and the fluence was in the range of 4-6 J/cm^2. The laser wavelength of 193 nm was chosen as suitable for these experiments after several trials [15]; the trials were performed using a Nd:YAG laser (at 1064 nm, 532 nm, 355 nm and 266 nm, 10 Hz repetition rate, similar laser fluences and spot area) and the previously mentioned excimer laser (at 193 nm). 50 000 laser pulses per sample were used, at a target-substrate distance of 5 cm; the substrates were kept at room temperature, with all depositions made in vacuum ($10^{-3} – 10^{-5}$ mbar).

2.3. Analysis

Thin films surface and roughness was investigated by atomic force microscopy (AFM) on several areas and dimensions, using a “Nomad” setup produced by “Quesant Instrument Corporation”. The scanning mode was performed in non contact mode, but tapping mode was also used due to the low root mean square roughness (RMS). Vibrating sample magnetometry has been performed for specific magnetic characterization, on a LakeShore setup. Optical investigations were made using a Zeiss Axio-Lab microscope at 100x and 200x magnification power; the same device was used to visualize the magnetic domains in the bulk alloy used as target, by magneto-optical Kerr effect (MOKE). SEM measurements were performed with an Inspect F FEG-SEM. The electron acceleration voltage can be set between 200 V and 30 kV; the lateral resolution is ~2 nm. Electrical properties of the thin films were investigated by an impedance analyzer (Agilent 4294A), at room temperature, in the range of 1 KHz – 2.5 MHz.

a.)



b.)

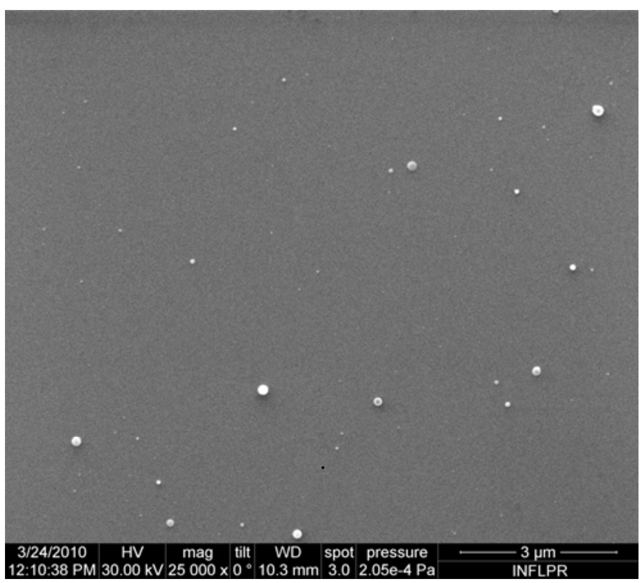
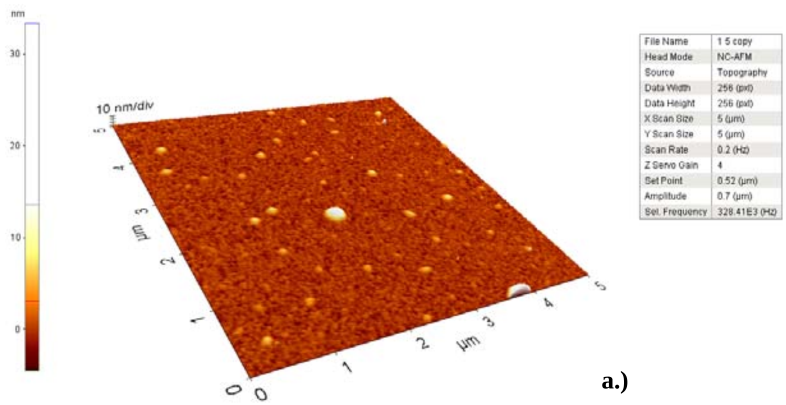
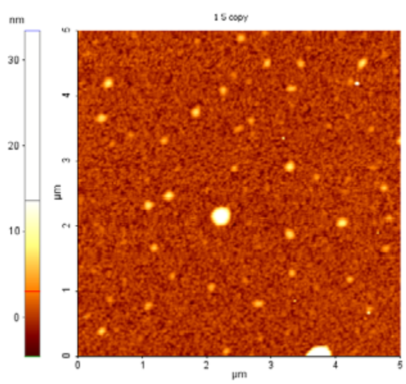
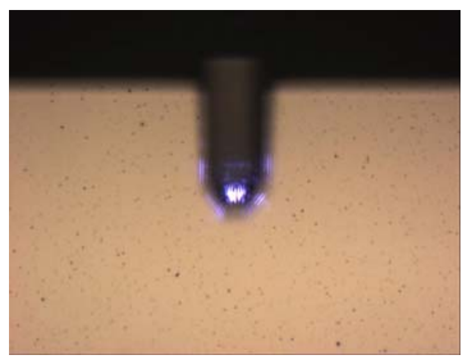


Fig. 3. SEM images of FeSi thin films on silicon (a) and quartz (b) substrates, deposited at 193 nm, 50 Hz, 4 J/cm^2



a.)





b.) c.)

Fig. 4. AFM images (a, b) and actual photograph of the scanned area taken by the microscope on board videocamera (c) for a FeSi thin film deposited on silicon substrate (193 nm, 50 Hz, 4 J/cm^2)

3. Results and discussion

As it can be seen in the SEM (figure 3) and in the AFM images (figure 4), the surfaces of the thin film samples are very smooth with very few droplets present; the droplets increase in number if the fluence is higher than 6 J/cm^2, if the laser spot area is smaller than 2 mm^2 or if the substrate's crystalline structure is incompatible with the one of the thin films (such is the case for quartz, BK7 glass and SITAL substrates).

The thickness of the thin films was found to be in the range of 200–250 nm, depending on the laser fluence, using a step that was scanned by AFM; the roughness of the films is in the range of 1,6–3,8 nm (for silicon, platinum covered silicon and quartz substrates) and in the range of 3,5–7,2 nm on the BK7 glass and SITAL ceramic substrates. The stoichiometry of the target is preserved in the thin films at all wavelengths used, as determined and explained elsewhere [15].

Electrical measurements on the thin films deposited on silicon and platinum covered silicon substrates revealed that the resistivity is about $1.9 \cdot 10^{-3}$ Ω·m (figure 5). Measurements made on the thin films deposited on the rest of the substrates (quartz, BK7 and SITAL) were not conclusive, due to large experimental errors.

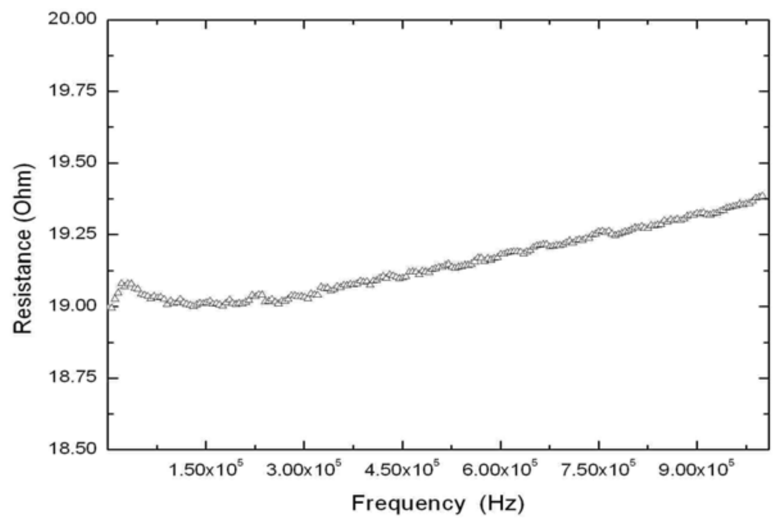


Fig. 5. Electrical measurements on a FeSi thin film on platinum covered silicon substrate

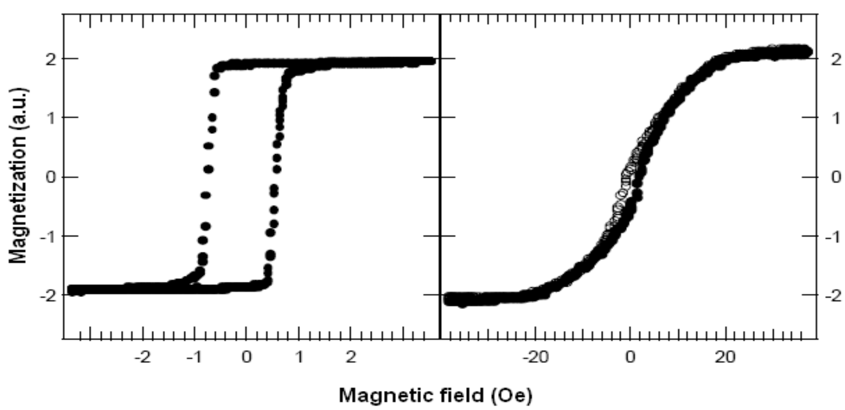
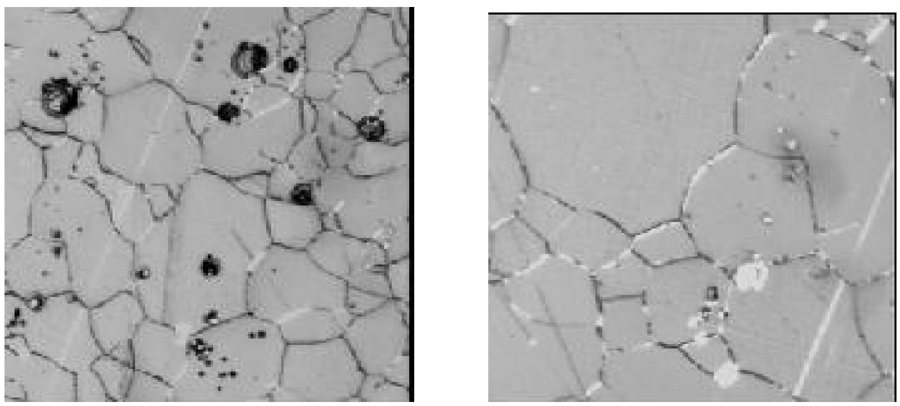


Fig. 6. Hysteresis loops for a FeSi sample deposited on silicon substrate on the easy magnetization axis (a) and on the hard magnetization axis (b) [J. Diaz et al., 2002]

Magnetic investigations on the FeSi thin films revealed no texture, but a difference in the shape of hysteresis loops with respect to the direction of applied field (figure 6). MOKE investigations on the target surface revealed well defined magnetic domains of different shapes and dimensions (figure 7); investigations were also made at the thin film surface of the deposited samples, but with inconclusive experimental results, possibly due to sample size.



a.) **b.)**

Fig. 7. Photographs taken by MOKE at 100x (a) and 200x (b) magnification power, revealing magnetic domain structures on the FeSi target (*courtesy of G. Epureanu*)

6. Conclusion

This paper demonstrates that good quality FeSi thin films can be achieved by pulsed laser deposition, on several types of substrates (silicon, platinum covered silicon and quartz). The AFM and SEM investigations correlate for the morphological characteristics and thickness of the thin films. Electrical measurements in thin films indicate similar values to those published in the literature, but for thin films developed by other techniques (e.g. sputtering), while the investigation of the magnetic properties reveal sharp hysteresis loops.

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REFERENCES

[1] *H. Gavrila, V. Ionita, P. Ciureanu, H. Chiriac, A. Yelon*, Technical and Applied Magnetism ("Magnetism tehnic si aplicat"), Romanian Academy Press, Bucharest (2000); in Romanian

[2] *T. Waeckerle, H. Gavrila, M. Marionpera*, "A method of describing magnetic behavior based on metallurgical features", Journal of Magnetism and Magnetic Materials 133 (1994) 101

[3] *H. Gavrila, V. Ionita*, "Crystalline and amorphous soft magnetic materials and their applications - Status of art and challenges", Journal of Optoelectronics and Advanced Materials 4 (2002) 173;

[4] *D. Jiles*, Introduction to magnetism and magnetic materials, CRC Press, ISBN 0412798603 (1998)

[5] *C. W. Chen*, Magnetism and metallurgy of soft magnetic materials, North-Holland Publishing Company, Amsterdam (1977)

[6] *J. Díaz, R. Morales, S.M. Valvidares, J.M. Alameda*, "Phase separation in Fe-Si and Co-Si sputtered ferromagnetic alloys and the origin of their magnetic anisotropy", Physical Review B 72 (2005) 144413

[7] *M. Walterfang, W. Keune, K. Trounov, R. Peters, U. Rücker, K. Westerholt*, "Magnetic and structural properties of epitaxial c-FeSi films grown on MgO (100)", Physical Review B 73 (2006) 214423

[8] *K. Akiyama, S. Ohya, S. Konuma, K. Numata, H. Funakubo*, "Composition dependence of constituent phase of Fe-Si thin film prepared by MOCVD", Journal of Crystal Growth 237 (2002) 1951

[9] *M. Tode, Y. Takigawa, M. Ohmukai*, "Hot-target laser ablation is critical for b-FeSi2 growth on Si without fragments", Metallurgical and Materials Transactions A 39A (2008) 130;

[10] S. *Uekusa, M. Yamamoto, K. Tsuchiya, N. Miura*, "Composition of beta-FeSi2 thin-films grown by a pulsed laser deposition method", Materials Research Society Symposium Proceedings 744 (2003) 309

[11] *T. Yoshitake, T. Nagamoto, K. Nagayama*, "Microstructure of beta-$FeSi_2$ thin films prepared by pulsed laser deposition", Thin Solid Films 381 (2001) 236

[12] *C. Constantinescu, N. Scarisoreanu, A. Moldovan, M. Dinescu, L. Petrescu, G. Epureanu*, "Thin films of NdFeB deposited by PLD technique", Applied Surface Science 253 (2007) 8192

[13] *C. Gheorghies, S. Condurache-Bota, M. Dinescu, C. Constantinescu, N. Cazacu*, "New reinforcing technique of alumina coatings on steel substrates", Optoelectronics and Advanced Materials – Rapid Communications 2 (2008) 569

[14] *C. Constantinescu, E. Morintale, N. Scarisoreanu, A. Moldovan, M. Dinescu*, "Nanometric-sized Fe/Pt thin films with perpendicular anisotropy developed by layer-by-layer pulsed lased deposition", Physics AUC 20 (2010) 73

[15] *E. Morintale, C. Constantinescu, M. Dinescu*, "Thin films development by pulsed lased-assisted deposition", Physics AUC 20 (2010) 43

[16] *Y. Makita, Y. Nakayama, Y. Fukuzawa, S.N. Wang, N. Otogawa, Y. Suzuki, Z.X. Liu, M. Osamura, T. Ootsuka, T. Mise, H. Tanou*, "Important research targets to be explored for β-$FeSi_2$", Thin Solid Films 461 (2004) 202

[17] *S.N. Wang, N. Otogawa, Y. Fukuzawa, H.L. Shen, H. Tanoue, T. Kojima, Y. Nakayama, Y. Makita*, "Prototype infrared optical sensor and solar cell made of beta-$FeSi_2$ thin film", Proceedings of SPIE 5065 (2003) 188

[18] *J.M. Ting, S.W. Hung, K.H. Liao*, "Characteristics of Fe-Si thin-film catalysts and their effects on the growth of carbon nanotubes", Journal of the Electrochemical Society 155 (2008) K146

[19] *J.B. Kim, H.Y. Lee, K.S. Lee, S.H. Lim, S.M. Lee*, "Fe/Si multi-layer thin film anodes for lithium rechargeable thin film batteries", Electrochemistry Communications 5 (2003) 544.