Microstructural characterization of nanocomposites produced by laser ablation in a magnetic field

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Abstract. We present a microstructural study of nanocomposite samples based on iron oxide and a noble or a transition metal. The samples were produced by laser ablation in air at atmospheric pressure in the presence of a magnetic field. This technology allows production of oriented nanowires composed by nanoparticles. We applied a simultaneous laser ablation of two targets in an external magnetic field. The targets used for the ablation were a magnetic material (iron) and a noble or a transition metal (silver, gold or cobalt). The presence of a magnetic field during the deposition results in arranging the nanoparticles formed in the plasma plume into micrometric nanowires on the substrate. The structural analyses confirm that the samples are composed by iron oxide and a noble or a transition metal.

1. Introduction

One important branch of studies in the field of nanotechnology is the fabrication of nanomaterials consisting of two or more distinct elements, such as alloyed, bimetallic and composite nanostructures [1–4]. Structures that integrate two distinct functionalities into a single unit have attracted particular interest; for example, systems consisting of a noble metal and a magnetic material [5–7]. Such materials can exhibit not only the properties associated with their single counterparts, but also may enhance some specific characteristics or even express new properties due to the synergistic effects induced by the interactions between the different components [8,9]. Therefore, these hybrid structures are very attractive for applications as catalysts, magnetic sensors, or in magneto-optics, optical detection, and biophotonics [2, 10–12].

Among the most common methods for fabrication of multicomponent nanostructures are sputter deposition, electroless plating, and also wet chemical, electrochemical, photochemical and sonochemical synthesis [13, 14]. The use of these techniques or combining any of them can lead to the formation of alloys, core-shell or dumbbell architectures [12, 14]. However, the abovementioned methods are mainly chemically-based and usually involve multistep processes, which hampers a potential large-scale industrial production of such structures.

As a physical method for fabrication of nanostructures, pulsed laser deposition (PLD) in the presence of a magnetic field shows some advantages [15, 16]. Unlike the classical PLD method, the deposition process here can take place in air at atmospheric pressure (open air), which avoids the need
for a vacuum system. The method has proved to be a promising way of producing oriented or/and composite nanostructures [15–18]. In this method, the application of an external magnetic field during the deposition process leads to the arrangement of the nanoparticles in the plasma plume, forming long nanowires predominantly oriented along the magnetic field lines. The PLD technology in a magnetic field has been developed for both fs- and ns-laser pulses. Despite the significant progress in understanding the influence of the processing conditions on the characteristics of the structures produced by PLD in a magnetic field, a detailed study of the microstructure in the case of nanostructure systems has not yet been made.

The aim of this work was to investigate the microstructure of composite nanostructures produced by PLD in a magnetic field. The samples were deposited by simultaneously ablation of two adjacent targets, one of which was always Fe and the other, Co, Ag or Au. The morphology, phase composition and crystallinity of the structures obtained are studied and discussed in detail.

2. Experimental

A schematic of the deposition process by PLD in an external magnetic field is shown in figure 1. The classical on-axis PLD configuration was modified by attaching a permanent magnet ($B = 0.4$ T) to the back side of a quartz substrate, so that the magnetic field lines were parallel to the substrate surface. The laser ablation was implemented by nanosecond pulses delivered by a Nd:YAG (Lotis LS-2147) laser system operating at a wavelength of 1064 nm. The targets used for the ablation process consisted of two plates, one of which was always Fe (99.99 %) and the other, Co (99.99 %), Ag (99.99 %) or Au (99.99 %). The laser radiation was focused on the plates so that the laser spots fell equally on both metals. The target was mounted on an XY translation stage to prevent drilling the target during the ablation. The laser fluence used in the ablation process was 3 J/cm$^2$. The material deposited on the substrates was produced by 6000 laser pulses. The depositions were carried out in open air at a target-substrate distance of 20 mm. The morphology of the obtained samples was studied by scanning electron microscopy (SEM) using a LYRA I XMU system (Tescan). The phase composition and crystallinity of the samples were investigated by an Empyrean diffractometer (PANalytical) through glancing (3°) incidence X-ray diffraction (GIXRD) using CuKα radiation. The crystalline phases were identified using the PAN-ICSD and COD databases cards. The quantitative phase composition of the samples and the average crystallite size were obtained by profile fitting of the existing phases using the HighScore Plus and ReX software [19, 20].

3. Results and discussion

Figure 2 shows SEM images of the structures produced by PLD in a magnetic field. The samples were deposited under identical process conditions, but using different ablation targets: (a) Fe, (b) Fe-Co, (c) Fe-Ag and (d) Fe-Au. The SEM analysis of the samples’ surface reveals the presence of nanowires which follow to a large extent the direction of the external magnetic field. These nanowires are composed by arranged nanoparticles and form elongated features with a length varying in the range from several microns to several tens of microns. As seen, the orientation effect of the nanowires is more pronounced in the structures that are deposited from magnetic materials (figure 2a,b), compared to the cases where one part of the target is a non-magnetic material (figure 2c,d). The use of magnetic targets also leads to the deposition of more material on the substrate due to the interaction of the ablated material with the external magnetic field. It is known that laser deposition in open air is very inefficient process due to the strong confinement of the ablated material [21]. Under such conditions, the nanoparticles are formed in the
plasma plume close to the target and their transfer to a substrate located at a distance of over 20 mm is practically impossible. However, when a magnetic material is ablated in the presence of a magnetic field, deposition at a target-substrate distance of 20 mm is easily achievable, as seen in figure 2. In this case, the magnetic nanoparticles formed in the plasma plume are attracted by the external magnetic field and deposited on the substrate.

Figure 2. SEM images of nanostructures deposited in a magnetic field by PLD from: (a) Fe, (b) Fe-Co, (c) Fe-Ag and (d) Fe-Au targets. The samples are deposited by 6000 pulses at laser fluence of 3 J/cm$^2$ and target-substrate distance of 20 mm.

Figure 3 presents XRD patterns of the structures shown in figure 2. The XRD pattern of the sample deposited from a pure Fe target shown in figure 3a reveals a phase composition that is a combination of two iron oxides – magnetite (ICSD 98-015-8741) and wüstite (ICSD 98-002-7237). As seen in table 1, the ratio between the two phases in the structure is Fe$_3$O$_4$ – 69% and Fe$_{1-x}$O – 31%. Table 1 also presents the average crystallite size of the phases for each sample in this study. For the structure in figure 2a, the average crystallite size of the predominant phase (magnetite) is 19 nm, which is almost the same as the size of the wüstite crystallites – 18 nm. It should be noted that no diffraction peaks for Fe are observed. Figure 3b is the XRD pattern of the sample deposited from the Fe-Co target. Magnetite is the only iron oxide identified in this XRD spectrum, while the wüstite phase is missing. The other phase that is supported by the spectrum is CoO (ICSD 98-000-9865). The predominant phase there is again Fe$_3$O$_4$ – 59%, with its crystallite size increasing to 23 nm in the presence of CoO. The average crystallite size of the CoO phase is 28 nm. The XRD pattern of the sample deposited from the Fe-Ag target is shown in figure 3c. The phases identified are Fe$_3$O$_4$ – 66%, Fe$_{1-x}$O – 25% and Ag – 9%. It should be emphasized that the Ag is present in the XRD spectrum as a separate phase (ICSD 98-018-0878). The average crystallite size of each phase in this sample is estimated as follows: Fe$_3$O$_4$ – 23 nm, Fe$_{1-x}$O – 15 nm, and Ag – 16 nm. Figure 3d shows the XRD pattern of the sample deposited from the Fe-Au target. The iron oxide phases identified in this spectrum are the same as in the samples deposited from pure Fe and Fe-Ag targets. As is the case with Ag, Au is identified as unbound (ICSD 98-004-4362). The precise phase composition of the sample is: Fe$_3$O$_4$ – 54%, Fe$_{1-x}$O – 39%, and Au – 7%. The average crystallite size of the Fe$_3$O$_4$ phase is 25 nm – the largest among all samples, while that of the Fe$_{1-x}$O phase is the smallest – 14 nm. The size of the Au crystallites is estimated at 21 nm.
Several key points in the results of the XRD analysis should be stressed. The material ablated from the Fe target is completely oxidized, which is confirmed by the absence of pure Fe peaks in the XRD patterns of the samples. The predominant phase in the samples studied is magnetite, which is a ferrimagnetic material. The ratio of the iron oxide phases (Fe$_3$O$_4$ and Fe$_{1-x}$O) in the sample changes depending on the other phase – Ag, Au or CoO. Furthermore, the average crystallite size of the two iron oxides also changes in the presence of another phase. It is found that the size of the Fe$_3$O$_4$ crystallites rises with the addition of Ag, Au or CoO in the system, while the inverse effect is observed for the wüstite phase. It should further be mentioned that the deposition of non-magnetic nanoparticles, such Ag and Au, at a distance of 20 mm is only possible if they adhere to the Fe$_3$O$_4$ nanoparticles, as this is the only phase with well-expressed magnetic properties.

**Table 1.** Phase composition and average crystallite size of the samples in this work.

| Targets | Phase composition (wt%) | Average crystal size (nm) |
|---------|-------------------------|---------------------------|
|         | Fe$_3$O$_4$ | Fe$_{1-x}$O | CoO | Ag | Au | Fe$_3$O$_4$ | Fe$_{1-x}$O | CoO | Ag | Au |
| Fe      | 69          | 31          | –   | –  | –  | 19          | 18           | –   | –  | –  |
| Fe-Co   | 59          | –           | 41  | –  | –  | 23          | 28           | –   | –  | –  |
| Fe-Ag   | 66          | 25          | –   | 9  | –  | 23          | 15           | 16  | –  | –  |
| Fe-Au   | 54          | 39          | –   | –  | 7  | 25          | 14           | –   | –  | 21 |

4. Conclusions

This paper presents a microstructural investigation of composite nanostructures produced by PLD in the presence of a magnetic field. The deposition of composite samples is implemented by the simultaneous ablation of Fe and Co, Fe and Ag, and Fe and Au targets. The XRD analysis confirms that each sample contains both target metals. The morphological analysis of the samples reveals that their structure consists of micrometric nanowires that predominantly follow the direction of the external magnetic field. However, the presence of the non-magnetic metals Ag and Au in the structure notably worsens the degree of nanowires’ orientation. The phase composition of the as-deposited samples is a combination of several phases, with Fe$_3$O$_4$ being the predominant one. Furthermore, the ratio of the Fe$_3$O$_4$ and Fe$_{1-x}$O phases in the sample depends on the other phase – Ag, Au or CoO. It is further found that the presence of the other phase in the sample leads also to an increase in the average size of the Fe$_3$O$_4$ crystallites and a decrease in the Fe$_{1-x}$O crystallite size. Both the largest crystallite size of the predominant phase – 25 nm, and the smallest crystallite size of the Fe$_{1-x}$O phase – 14 nm, are observed in the sample with Au. The largest crystallite size among all samples is that of CoO – 28 nm, while the Fe$_{1-x}$O phase in this sample is completely absent.

Acknowledgements

This work was partially supported by the Bulgarian Ministry of Education and Science under the National Research Program "Young scientists and postdoctoral students" approved by DCM # 577/17.08.2018.
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