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LETTER TO THE EDITOR

Synthesis of nanocrystal films via femtosecond laser ablation in vacuum

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Abstract

A new technique based on ultrashort laser ablation of solid targets in vacuum was used to synthesize films of individual nanocrystals of magnetic atoms (Fe and Ni). Laser pulses of 300 fs at 527 nm were used to produce a plume mainly constituted of nanoparticles of the target materials. After vacuum expansion, the plume was deposited on substrates at room temperature to produce $\approx$1 μm thick films. Atomic force microscopy and x-ray diffraction analyses of the deposited samples have demonstrated the possibility of producing films constituted of high quality, individual nanocrystals of the atomic targets, with an average size of $\approx$20 nm, and a narrow size distribution. The ultrashort laser ablation and vacuum deposition proved to be a very versatile and simple technique for obtaining nanocrystal films of different materials.

1. Introduction

The synthesis and analysis of nanoparticles (NPs) of various elements and compounds is receiving increasing attention because of its significance both in fundamental research and in technological applications [1, 2]. Reasons for such interest in NPs and films made of aggregates of NPs are based on the physical properties associated with their small size and the large surface-to-volume ratio. These lead to peculiar properties that cannot be found in corresponding bulk materials [3, 4].

Different techniques have been used for NP production, such as arc discharge, vapour and electrochemical deposition, sputtering and laser ablation with long, nanosecond pulses in an appropriate background gas. More recently, femtosecond laser ablation in vacuum has

been suggested as a powerful and versatile tool for the production of metal and semiconductor nanoparticles [5–8]. As an NP synthesis technique, ablation in vacuum with ultrashort laser pulses is attractive for several reasons. First, femtosecond laser pulses do not interact with the ejected particles, thus avoiding complicated secondary laser–material interactions. Second, for femtosecond laser pulses the initial laser-heating occurs almost at solid density, thus leading the matter to extreme temperature and pressure, and generating novel material states which cannot be produced by using longer pulses of comparable fluence. It is, thus, ideal for studying the fundamental properties of matter under extreme conditions and the physics related to the relaxation from these states. Third, it is easily applied to a wide range of materials, and for appropriate conditions it can retain the stoichiometry of the target in the produced particles [9, 10]. Finally, since the plume expansion takes place in vacuum, all the complications introduced by the presence of a background gas are avoided.

Previous studies have mainly concentrated on the analysis of the plasma plume produced during femtosecond laser ablation and on the size characteristics of the produced NPs, measured by atomic force microscopy analysis of less than one layer deposits of the ablated material [5, 6, 8]. Here we show the possibility of using this technique to deposit films of high quality nanocrystals in the specific case of magnetic atoms, because of their broad scientific and technological interest. In particular, we have investigated the characteristics of Fe and Ni nanocrystals synthesized via ultrashort pulsed laser deposition (uPLD) in vacuum, when they are aggregated to form a film of NPs, and we have demonstrated the possibility of producing films of individual NPs sticking to one another via electrostatic and van der Waals forces. The morphological and structural properties of the NP films have been investigated by atomic force microscopy and x-ray diffraction. The sizes and size distributions of individual nanocrystals of the films have been measured and compared with those obtained from less than one layer deposits. Although a detailed analysis has been carried out only on magnetic atoms, other elemental targets (noble metals and Si, in particular) and also compound targets (e.g., terfenol ($Tb_{0.3}Dy_{0.7}Fe_2$)) are under investigation. Preliminary results clearly indicate that this ultrashort laser ablation and vacuum deposition technique can be a very versatile and simple way of obtaining nanocrystal films of different materials, and it also has the ability of retaining the stoichiometry of complex solid targets in the produced films.

2. Experimental setup

The experimental apparatus is very similar to that used in our previous work on ultrashort laser ablation and deposition of different materials [4–6]. Laser ablation experiments were carried out by using laser pulses of $\approx$1 mJ–300 fs at 527 nm, obtained by second-harmonic-generation pulse compression of the Nd:glass $\approx$ 1 ps fundamental output at 1055 nm. The temporal profile of the pulse was checked in real time by a single shot background-free autocorrelation technique. The laser radiation was focused to a spot size of $\approx 7 \times 10^{-4}$ cm^2 on the sample surface, at an incident angle of 45°, and in p-polarization. The laser pulse energy was varied by means of calibrated attenuating plates. The target was mounted on a rotating holder to minimize pit formation, and placed in a vacuum chamber evacuated to a residual pressure of 10^{-7} mbar.

Films were produced by collecting the ablated material onto substrates located about 30 mm away from the target surface and held at room temperature. The present results were obtained with 99.9% pure iron and nickel as prototype targets, although preliminary experiments on noble metals, and multi-component materials have also been carried out. The morphology of the deposited films was analysed at various stages of the deposition process by atomic force microscopy (AFM). The AFM images were collected in tapping mode (scan rate 1 Hz, scan size 1 μm) by using a sharpened silicon tip with a radius of less than 5 nm. In

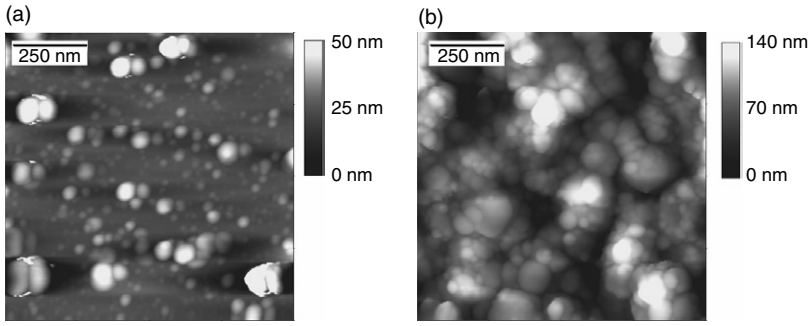

Figure 1. AFM images of nickel nanoparticles: (a) less than one layer deposit; (b) film.

particular, less than one layer deposits on freshly cleaved mica substrates were considered to measure the sizes of the NPs produced during the femtosecond laser ablation process, while the size of the NPs in the aggregate films were obtained by AFM analysis of the film surface at different stages of the deposition process. Finally, the structural analysis of the deposited films was performed by x-ray diffraction (XRD), using the typical Bragg–Brentano powder geometry.

3. Results

Figure 1 shows two AFM images of less than one layer (a) and many layers (b) of nickel nanoparticles, deposited at a laser fluence of 0.4 J cm^{-2} and at a repetition rate of 33 Hz. Panel (a) shows a large number of disperse NPs and some islands where NPs have stuck together. For less than one layer samples, the sizes of the isolated NPs range from a few nanometres to tens of nanometres. Panel (b) refers to a film of NPs with a thickness of 350 nm. The density of NPs in the film appears rather large, with most individual NPs sticking to one another. However, where the NP density is thinner, it is possible to observe and measure the size of individual constituent NPs, and the sizes result in being fairly similar to those obtained for isolated NPs in less than one layer deposits. Similar images were obtained for films of different thicknesses ranging between 0.2 and 2 μm, indicating a good uniformity of the morphology in the volume of the deposit. Similar results were obtained in the case of iron. Therefore, we can conclude that the basic structure of the films deposited by ultrashort laser ablation in vacuum, and at room temperature, is that of a cauliflower-like, granular agglomerate of nanoparticles sticking to one another, while maintaining their own individuality.

Figure 2 shows representative size distributions of the NPs obtained by AFM images of less than one layer deposits of NPs produced during laser ablation of nickel (left panel) and iron (right panel) targets. The size distributions show very similar characteristics for the two materials, with a peak at 10–15 nm and a tail extending up to 50–60 nm. The size distribution is fairly well described by a lognormal function (full line) in both cases [11]. The mean radius $\langle R \rangle$ and the geometrical standard deviation σ_g result in being $\langle R \rangle = (15.8 \pm 0.9)$ nm and $\sigma_g = (0.67 \pm 0.05)$ for nickel, and $\langle R \rangle = (18.7 \pm 0.8)$ nm and $\sigma_g = (0.60 \pm 0.04)$ for iron, respectively.

In the case of nickel, samples were produced at various laser fluences to investigate the effect of the laser energy on the NP size. The results of such a characterization showed that most NPs have a radius ranging from a few nanometres to 50 nm, with a quite modest up-shift of the mean radius and maximum size as the fluence increases. Therefore, within the

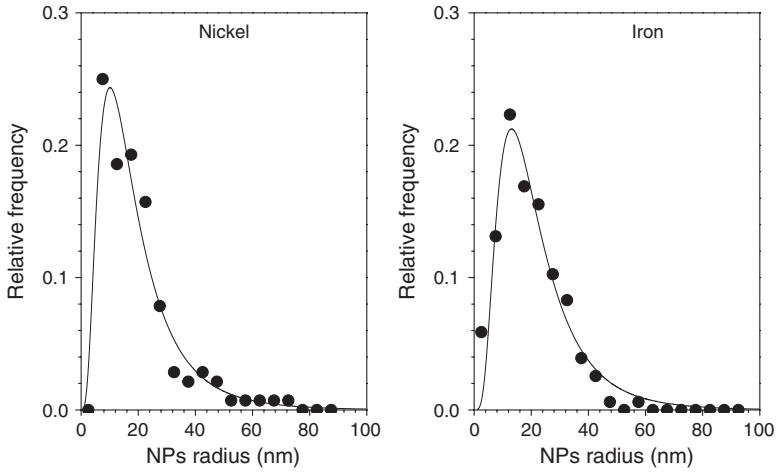

Figure 2. Representative size distributions of nickel (left panel) and iron (right panel) nanoparticles.

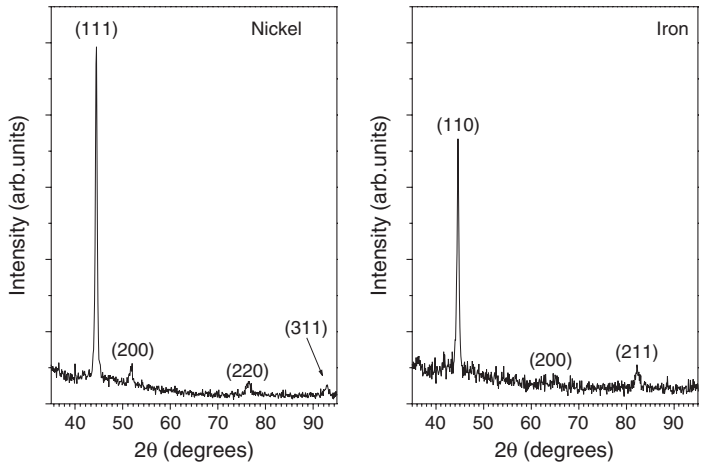

Figure 3. XRD pattern of NP films of nickel (left panel) and iron (right panel).

limits of the experimental errors and of a limited statistics, we can conclude that the sizes of the produced NPs do not show significant changes with the laser fluence from the ablation threshold ($\approx$0.1 J cm^{-2}) up to $\approx$1 J cm^{-2}. On the other hand, the film deposition rate increases with the fluence passing from $\approx$0.1 nm s^{-1} at 0.4 J cm^{-2}, to $\approx$0.25 nm s^{-1} at 1.1 J cm^{-2}.

Figure 3 shows the typical x-ray diffraction patterns obtained from nanogranular films of nickel (left panel) and iron (right panel), respectively, in the same experimental conditions of figure 1(b). Diffraction peaks are clearly observed and are located at positions consistent with those expected for the elemental target materials. If one considers that the diffracted intensity tends to decrease with the 2θ angle because of the effect of the limited thickness of the film, the diffraction pattern does not disclose significant textures. Once corrected for the film thickness effect, the relative peak intensities are close to those of the corresponding powder standards, pointing out that both Ni and Fe films are mostly composed of random oriented nanocrystallites. The analysis of the peak widths using the well-known Scherrer

formula indicates that diffraction comes from crystallites with a size of few tens of nanometres, which is totally consistent with the sizes of the nanoparticles derived by AFM imaging analysis: particles observed at the AFM are likely to be made of single-crystalline domains. We can thus safely conclude that the technique of femtosecond laser ablation and deposition in vacuum successfully leads to the production of nickel and iron films of randomly oriented individual nanocrystals.

4. Conclusions

In conclusion, we have studied the synthesis and properties of NPs and NP films produced by laser ablation of elemental magnetic materials (nickel and iron) with femtosecond laser pulses. Ablation was carried out in vacuum and the nanoparticles were deposited onto suitable substrates at room temperature. The properties of the deposited films were analysed by AFM and XRD techniques. AFM images were made of the deposits at various stages of the growth process, and the sizes of individual nanoparticles in the final films were measured and compared with the dimensions of the particles obtained by less than one layer deposits, resulting in fairly good agreement. Our findings show that the films have a cauliflower-like, granular structure with the constituting NPs mutually agglomerated while largely maintaining their own individuality. On the other hand, the XRD analysis of the samples showed that the films are composed of randomly oriented nanocrystals of the elemental target materials, the dimensions of which result of the same order of the NP size as determined by AFM. Our results thus indicate that ultrashort laser ablation and deposition in a vacuum lends itself as a simple and versatile synthesis technique for producing films of individual nanocrystals of different materials. We are currently extending the synthesis and characterization to other elemental and compound materials. Preliminary measurements clearly indicate that the results here obtained in the specific case of Fe and Ni can be more generally extended to other atomic elements, and that the femtosecond laser ablation/deposition technique is also able to produce deposits retaining the stoichiometry of a complex solid target, thus strongly supporting the possibility of its more general use with various materials of scientific and technological interest.

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