

All-self-assembled MgO nanorods and nanowires grown on Au-decorated MgO substrates by pulsed laser deposition

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We report on the fabrication of MgO nanorods and nanowires by a novel, all-self-assembled method, using Pulsed Laser Deposition. The seeds for the formation of these one-dimensional nanostructures consisted of self-assembled gold nanodots. Gold was used due to its well-known catalytic effect. Dimensions and surface density of the Au nano-dots, investigated by Atomic Force Microscopy, depend on the deposition conditions and the number of laser pulses. Morphology of the MgO nanorods and nanowires was investigated by SEM, and was found to depend strongly on the deposition conditions and on the architecture of the Au nanodots on the decorated substrates.

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1. Introduction

One-dimensional nanostructures have been recently investigated because they are promising nanoscale building blocks for nanodevices in electronics [1-3], photonics [4,5] and ultrasensitive biomolecular sensors [6,7]. Till recently, conventional semiconductors have been mostly studied as nanowire materials. Integrating more functionality into the nanowires by using other functional materials could allow for advanced nanowire devices in the future. For instance, transition metal oxides are known to exhibit a rich variation of physical properties, such as superconductivity, ferromagnetism and ferroelectricity.

MgO is an important material for use in catalysis, insulating layers in tunnel magnetoresistance junctions, etc, and as substrates for thin films of many transition metal oxides, including magnetite, other spinel ferrites, and perovskite oxides. MgO nanowires have been mainly fabricated by catalysis-assisted chemical vapour deposition [8]. Pulsed Laser Deposition (PLD) is one of the most powerful techniques to fabricate various functional material oxide thin films and heterostructures. Thus the feasibility of the PLD technique to fabricate various oxide nanowires will contribute to the integration of rich oxide functionalities into nanowires via in situ construction of oxide heterostructures in the nanowires. In the case of superconducting thin films, MgO nanorods and/or nanowires can act as effective magnetic flux

pinning centres, since it was found that even micron-sized defects (holes) can preferentially trap two flux lines before any vortex enters the superconducting film matrix [9]. Quite recently, the growth of MgO nanowires by PLD was reported on substrates with a Au catalyst sputtered through a metallic mask [10, 11].

Here we report on all-self-assembled MgO nanorods and nanowires grown by PLD on MgO (100) single crystal substrates decorated by PLD (a very few laser pulses) with Au nanodots. This type of substrate decoration was previously used for the creation of artificial pinning centres in superconducting films [12-17]. We show that the dimensions and density of nanorods/nanowires strongly depend on the deposition conditions and on the size and surface density of the self-assembled Au nanodots.

2. Experimental

In the first instance, ultrathin (1-2 nm) gold was deposited on MgO single crystal substrates at room temperature by thermal evaporation through a shadow mask so that a comparison could be made between regions with and without Au. Later, an Au target at 55 mm distance from the substrate was irradiated in-situ with 3 - 25 laser pulses at 1 Hz in 0.6 mbar O₂ at 800°C by a Lambda Physik LPX200 KrF excimer laser with a wavelength of 248 nm. In both cases 5 min at 800°C was

allowed after deposition for the Au to form into nano-dots before depositing 3000-120000 pulses of MgO at 10 Hz in an O₂ partial pressure of 0.13 -0.6 mbar with a target to substrate distance of 47 mm, also at 800°C. Laser fluence was 2.16J/cm² throughout the experiments, with a spot size of 7.5 mm².

A DI Multimode Nanoscope III Atomic Force Microscope (AFM) has been used in the tapping mode to study the morphology of the Au nanodots, using ultra-sharp AFM tips with diameter of curvature of 1 nm. The AFM pictures were analysed using WSxM 4.0 software. A JEOL 7000 Scanning Electron Microscope (SEM) was employed to observe the specimens at angles of 0° and 70° from the normal to the substrate.

3. Results and discussion

By a relatively small number of laser pulses on the gold target an incomplete layer is grown, consisting of nano-scale islands (nanodots). Their dimensions and surface number density depend on the target material used, on the type of substrate, and on the deposition conditions (substrate temperature, pressure and composition of the atmosphere in the chamber). In the case of ultrathin Au layers evaporated through the shadow mask, raising the temperature to 800 °C for the growth of MgO quite probably led to a change in morphology (the ultrathin gold layer self-assembled into large nanodots as recently reported for the case of Au on CeO₂ buffered sapphire [16]).

Fig. 1 shows an example of the decorated substrate morphology for the case of 5 laser pulses on the gold target after 5 mins at 800 °C post-deposition. As can be seen, there is a large number of very small gold nanodots on the MgO single crystal substrate, randomly distributed, with an average diameter of about 7 nm, and an average height of about 1 nm. Although at large enough scales it appears to be an approximately uniform surface density, there are a few regions in which some agglomeration of Au nanodots occurs, marked with an arrow in figs. 1b and 1c. Fig. 2 show AFM images of self-assembled gold nanodots on the substrate for 25 laser pulses on the gold target, again after post-deposition annealing at 800 °C for 5 mins. It can be seen that, in this case, the number density is higher, and the nano-dots are larger, 10-15 nm diameter and 2-3 nm height.

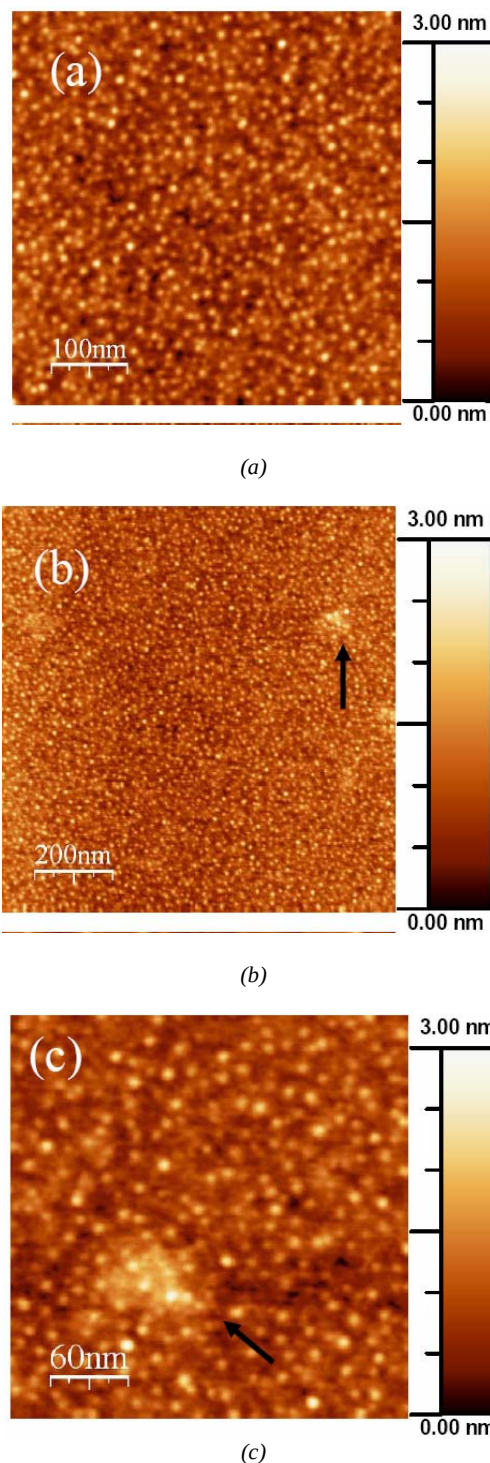
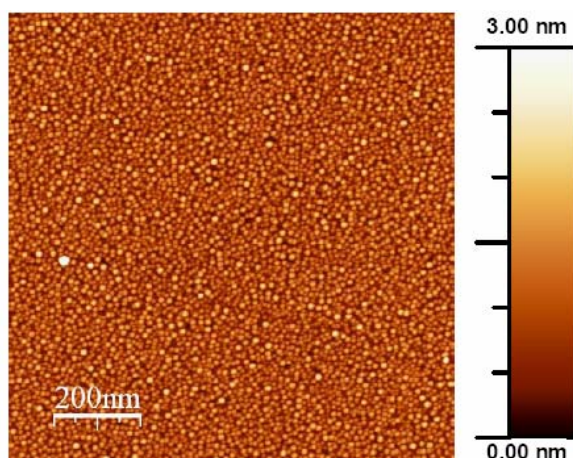


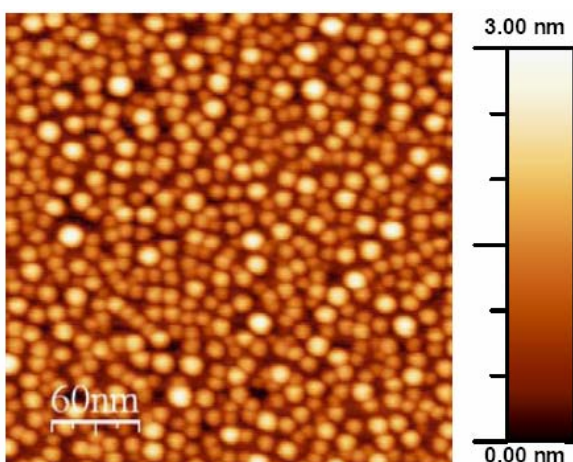
Fig. 1. AFM images of the MgO substrate decorated with 5 laser pulses on the gold target, at various magnifications. Arrows in (b) and (c) indicate a region where an agglomeration of Au nanodots occurred.

As previously mentioned, we have first investigated the growth of MgO on samples partially covered with ultrathin layers of gold, deposited by thermal evaporation using a shadow mask. In this way, the substrates have

regions without gold, and regions with large, thermally self-assembled Au nanodots.



(a)



(b)

Fig. 2. AFM images of the MgO substrate decorated with 25 laser pulses on the gold target, at two magnifications.

In the SEM image of Fig. 3 a great difference can be seen between the growth of MgO by PLD on such two different parts of the substrate. In more detail, the morphology of MgO in the two regions is shown in Fig. 4 (for the part of the substrate without Au), and in Fig. 5 (for the part of the substrate covered with Au) at a larger magnification. It can be seen that, in these deposition conditions, the top of the rather thick MgO layer (120000 laser shots) grown on bare substrate has a plate-like, disoriented morphology. In addition, several large boulders can be seen. In the case of MgO grown on the part of the substrate covered with the ultra-thin Au layer, the morphology of MgO is completely different. In figure 5, MgO grown on the substrate covered with the ultrathin

Au layer is composed mainly of cuboids having the base dimension up to 300-400 nm (hence, the name *nanorods*), and length up to a 1-2 microns.

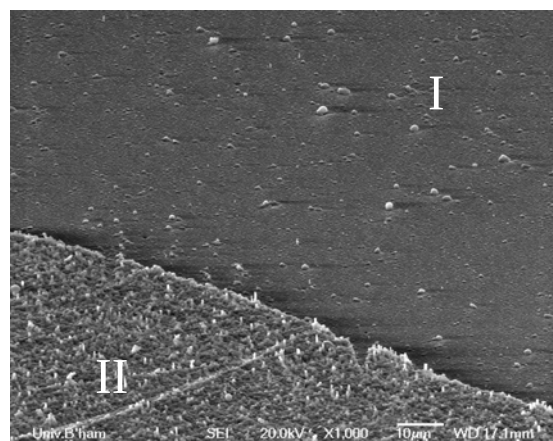


Fig. 3. SEM image (at 70° orientation) of MgO grown by 120000 laser pulses, in 0.13 mbar oxygen, on bare MgO single crystal substrate (region I) and on the part of the substrate with 2 nm evaporated gold (region II).

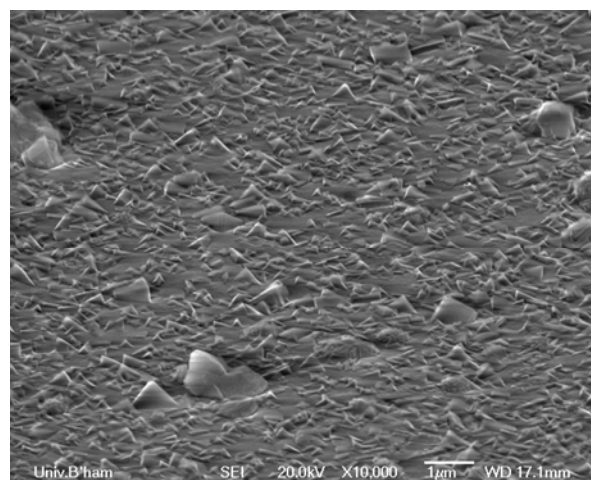


Fig. 4. SEM image at a larger magnification (top view) of the morphology of MgO grown on bare substrate (region I in fig. 2).

Of course, the length can be controlled by the number of laser pulses on the MgO target, but, as can be seen, they have quite different lengths, most likely due to the difference in dimension and heights of the thermally self-assembled Au nanodots. Most of the cuboids have grown perpendicular to the substrate, but there is still a large number of crystals that have an inclined orientation.

Apart from the architecture of the gold decorating the substrates, the most crucial parameter that needed careful adjustment for the formation of MgO nanorods and

nanowires was the oxygen partial pressure, that has a very narrow optimal window of 0.1 – 0.25 mbar.

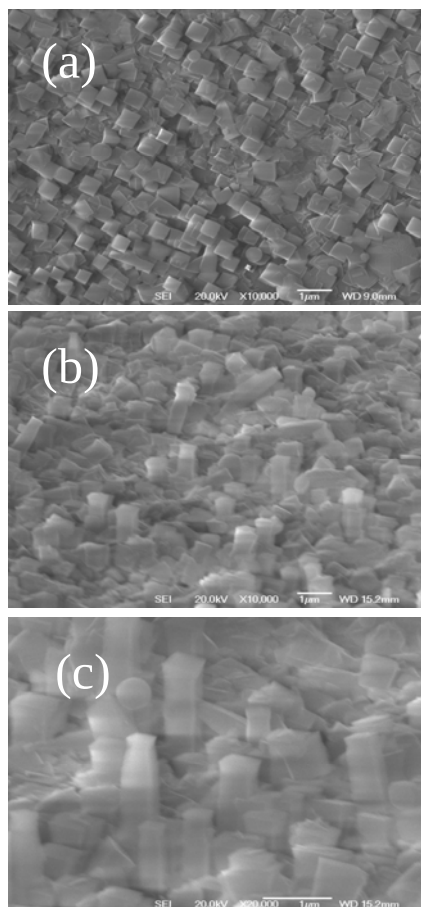


Fig. 5. SEM images at larger magnifications of the morphology of MgO grown on the part of the substrate with 2 nm evaporated gold (region II in fig. 2), top view (a) and 70° orientation (b,c).

On MgO substrates decorated with gold nanodots deposited by PLD we were able to grow long MgO nanowires. We are making the distinction between nanorods and nanowires based on their aspect ratio. Figure 6 shows SEM images at various magnifications of MgO nanowires grown by 120000 laser pulses in 0.16 mbar oxygen partial pressure on the MgO substrate decorated with 25 laser pulses of gold. As can be seen, MgO nanowires grown in these conditions have a square cross-section with dimensions of about 100 nm, and lengths of 1 – 2 µm. MgO nanowires that are not perpendicular to the substrate were possibly broken away from the substrate during the massive gas flow in the chamber prior to sample removal. Some large agglomerates (boulders) of MgO having spherical shape can also be seen, and most likely they are large particles resulted from the ablation process. The formation of these large boulders might also be related to some gold agglomerates on the substrate (like in figs 1 (a) and (b)), but this is quite unlikely since most of them are not in contact with the substrate.

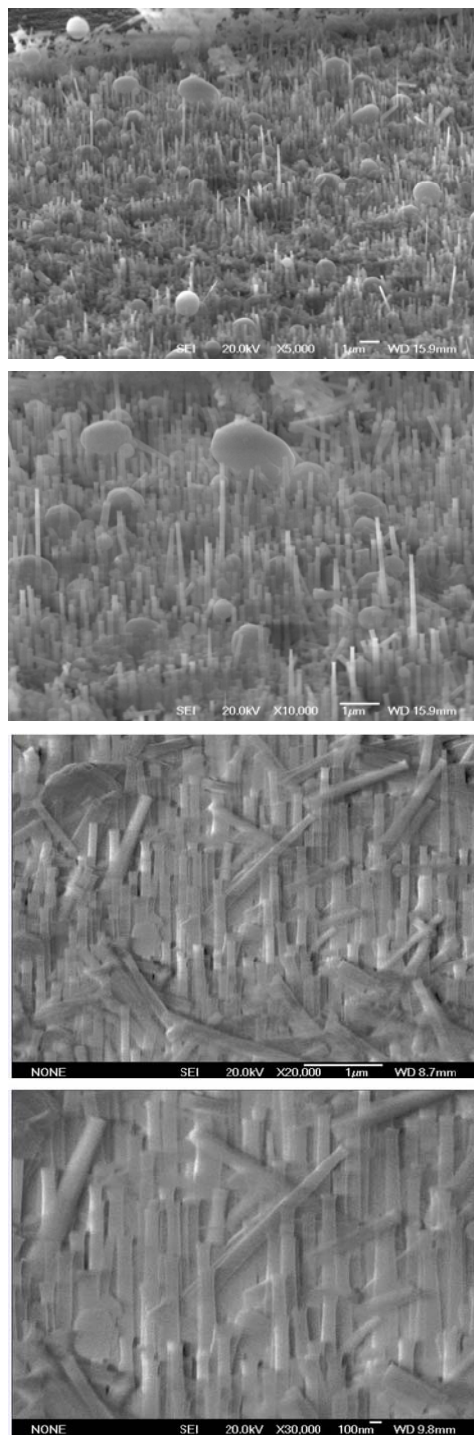


Fig. 6. SEM images (70° orientation) at 5000×, 10000×, 20000× and 30000× magnifications of MgO nanowires grown on substrate decorated with 25 laser pulses of Au.

On substrates decorated with a smaller number of laser pulses on the Au target, the architecture of gold nanodots led, in the optimum conditions of MgO growth, to the formation of much thinner MgO nanowires, with dimension of about 10 – 20 nm.

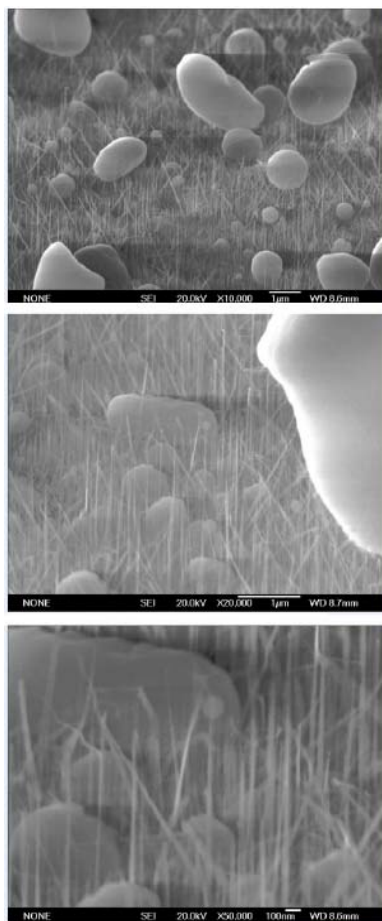


Fig. 7. SEM images (70° orientation) at 10000x, 20000x and 50000x magnifications of MgO nanowires grown on substrate decorated with 5 laser pulses of Au.

Fig. 7 shows SEM images, at various magnifications (10000x, 20000x and 50000x) of MgO nanowires grown by 60000 laser pulses in 0.16 mbar oxygen partial pressure on a substrate decorated with 5 laser pulses on gold target, like the one shown in Fig.1. Large boulders similar to those in Fig. 6 are also seen in this figure.

In conclusion, we have used pulsed laser deposition for growing MgO nanorods and nanowires by using the catalytic effect of gold. We have investigated the deposition conditions for the growth of these nanostructures and found that partial oxygen pressure is a key parameter. SEM images have shown that, on ultrathin gold layers deposited by thermal evaporation on the MgO substrates, subsequently deposited MgO by PLD grows in the shape of nanorods with square cross-section and planar dimensions of 300 – 400 nm. Thinner nanostructures were obtained on substrates decorated with Au nanodots, also grown by pulse laser deposition. In this case, the dimensions of MgO nanowires are determined by the architecture of Au nanodots. On substrates decorated with 25 laser pulses of gold, MgO nanowires have dimensions of the order of 100 nm, while on substrates decorated with 5 laser pulses of gold, nanowires are much thinner, of 10 – 20 nm. Their length is controlled by the number of laser pulses on the MgO target. In comparison with previously

reported growth of MgO nanowires by PLD, we have eliminated the need of using a very fine mesh for the deposition of gold catalyst [10, 11] by employing self-assembled gold nanodots whose dimensions and mean surface density were adjusted by the growth conditions.

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