



HAL
open science

Aligned three-dimensional prismatic magnesium nanostructures realized onto silicon substrate

Kaili Zhang, Carole Rossi, Christophe Tenaillieu, Pierre Alphonse

► To cite this version:

Kaili Zhang, Carole Rossi, Christophe Tenaillieu, Pierre Alphonse. Aligned three-dimensional prismatic magnesium nanostructures realized onto silicon substrate. *Applied Physics Letters*, 2008, 92 (6), pp.063123. 10.1063/1.2883934 . hal-03590671

HAL Id: hal-03590671

<https://hal.science/hal-03590671>

Submitted on 28 Feb 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Open Archive Toulouse Archive Ouverte (OATAO)

OATAO is an open access repository that collects the work of Toulouse researchers and makes it freely available over the web where possible.

This is an author-deposited version published in: <http://oatao.univ-toulouse.fr/>
Eprints ID : 2372

To link to this article :

URL : <http://dx.doi.org/10.1063/1.2883934>

To cite this version : Zhang, Kaili and Rossi, Carole and Tenailleau, Christophe and Alphonse, Pierre (2008) [*Aligned three-dimensional prismatic magnesium nanostructures realized onto silicon substrate.*](#) Applied Physics Letters, vol. 92 (n° 6). 063123. ISSN 0003-6951

Any correspondence concerning this service should be sent to the repository administrator: staff-oatao@inp-toulouse.fr

Aligned three-dimensional prislake magnesium nanostructures realized onto silicon substrate

Kaili Zhang,^{1,a),b)} Carole Rossi,^{1,a),c)} Christophe Tenailleau,² and Pierre Alphonse²

¹LAAS-CNRS, Université de Toulouse, 7 Ave du Colonel Roche, 31077 Toulouse, France

²CIRIMAT, 118 Route de Narbonne, 31062 Toulouse, France

(Received 8 January 2008; accepted 30 January 2008; published online 15 February 2008)

A simple approach is proposed to realize three-dimensional (3D) prislake Mg nanostructures, which has several advantages over previous investigations such as suitable for mass production, reduced impurities, tailored dimensions, and easier integration into microsystem. 3D Mg nanostructures are realized onto silicon substrate using a conventional thermal evaporator, where the incident angle of Mg vapor flux with respect to the substrate surface normal is fixed at 88°. The as-prepared 3D Mg nanostructures are characterized by scanning electron microscopy, x-ray diffraction, energy dispersive x-ray analysis, transmission electron microscopy, high-resolution transmission electron microscopy, and surface area measurement. © 2008 American Institute of Physics. [DOI: 10.1063/1.2883934]

Nanometal structures have received steadily growing interests because of their fascinating properties and various applications.^{1,2} As one of the most interesting alkaline-earth metals, magnesium has found applications in numerous fields such as hydrogen storage,^{3–6} battery,⁷ biochemistry,⁸ and organic synthesis,⁹ where hydrogen storage has been paid special attention. Magnesium dihydride (MgH₂) contains 7.6 wt % hydrogen, making it one of the most promising hydrogen storage materials. Although Mg nanoparticles prepared by the thermal decomposition of magnesium anthracene and sputtering^{10–12} and Mg nanocomposites synthesized by high-energy milling methods^{13–18} have been intensively investigated, there are few studies on one-dimensional (1D), two-dimensional (2D), and three-dimensional (3D) Mg nanostructures. Recently, Li *et al.* have synthesized 1D Mg nanorods/wires by a vapor-transport approach using commercially available Mg powder and addressed their interesting applications in Mg/air battery and hydrogen storage.^{19,20} However, there is no report in the literature to realize aligned 2D/3D Mg nanostructures. It is well-known that 2D/3D nanostructures are important components for nanoscale devices with a variety of applications due to their large surface areas and other unique properties.^{21–24} Therefore, it will be very promising to realize 2D/3D Mg nanostructures. In this study, the authors present a simple approach to realize aligned 3D prislake single-crystal Mg nanostructures onto silicon substrate using a conventional thermal evaporator. The as-prepared 3D prislake Mg nanostructures are characterized by scanning electron microscopy (SEM), x-ray diffraction (XRD), energy dispersive x-ray analysis (EDX), transmission electron microscopy (TEM), high-resolution TEM (HRTEM), and surface area measurement.

The 3D prislake Mg nanostructures are fabricated by a conventional thermal evaporator using 99.99% pure Mg pellets as the source material. The source holder is an alumina crucible that is heated by a tungsten filament. The substrate

is half of a 4 in. *p*-type (100) single-crystal silicon wafer. Before deposition, the substrate is cleaned using acetone, RT2 (chromic sulfuric acid mixture), thoroughly rinsed by de-ionized water and blow dried by nitrogen. Then, the substrate is placed into an oven at 200 °C for 20 min for further drying. The substrate is mounted into a specific movable substrate holder inside the evaporation chamber. The incident angle of Mg vapor flux with respect to the substrate surface normal is fixed at 88°. The distance between the substrate and the source is about 18 cm. After the chamber is evacuated to a vacuum level of 7×10^{-6} mbar, the evaporation of Mg starts with a constant supply current of 23 A. The deposition rate is set to be 5 Å/s and the deposition time is set as 800 s typically. The temperature of the substrate is around 45 °C during the deposition. The as-deposited Mg nanostructures on the substrate are directly characterized by SEM. To remove the effect of the well-crystallized silicon substrate, the Mg nanostructures are scratched from the substrate and then characterized with XRD and EDX. For TEM and HRTEM observations, the Mg nanostructures are manually separated from the substrate, mixed with ethanol, and deposited onto carbon-coated copper grids.

Figure 1(a) shows a top view SEM image of the Mg nanostructures. Roughly, the top view surface of most of the nano-Mg is hexagonal. Figures 1(b) and 1(c) are 30° tilted view SEM images taken at different directions confirming the 3D structure of the nano-Mg. As shown in Fig. 1(b), the borders of the nano-Mg are transparent due to the very small thickness. Figures 1(d) and 1(e) are cross-sectional view SEM images of the nano-Mg taken at different directions. Most of the 3D prislake Mg nanostructures are vertically aligned along the substrate surface. The length of the nano-Mg is around 1.2 μm. There are smaller and shorter structures among the long Mg nanostructures, as can be seen from Figs. 1(a)–1(e). The dimensions of the Mg nanostructures can be tailored by controlling the deposition conditions. For instance, Fig. 1(f) shows a cross-sectional view SEM image of the Mg nanostructures with a deposition time of 400 s. The resulting length of the nano-Mg is about 0.7 μm.

Atomic shadowing and adatom diffusion are the dominant growth mechanisms that control the 3D prislake Mg

^{a)} Authors to whom correspondence should be addressed.

^{b)} Electronic mail: kaili_zhang@hotmail.com.

^{c)} Electronic mail: rossi@laas.fr.

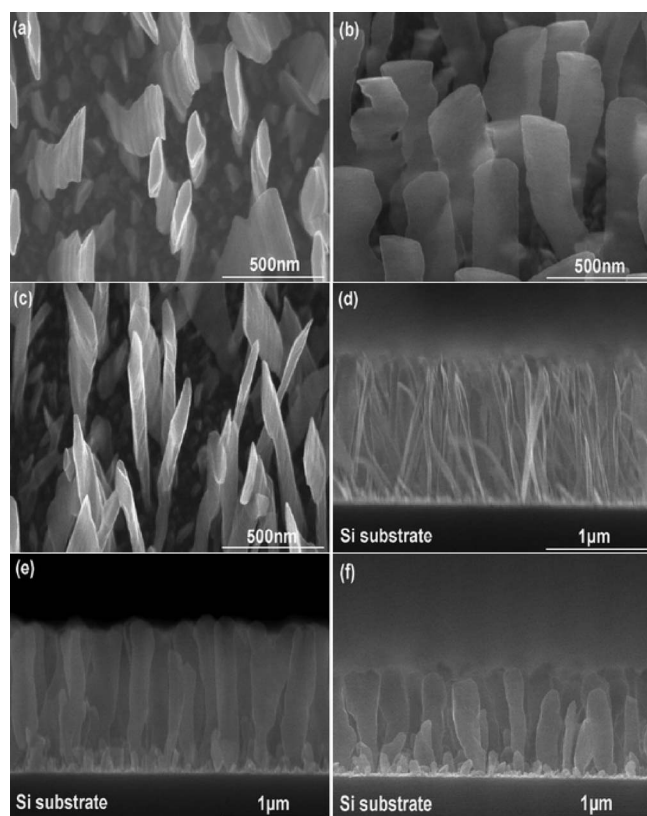


FIG. 1. SEM images of the as-prepared 3D prismatic Mg nanostructures.

nanostructures growth.²⁵ During deposition, some initial Mg nuclei are first formed on the substrate surface. These nuclei produce areas that the subsequent Mg vapor flux cannot reach directly due to atomic shadowing at high incident angles with respect to the substrate surface normal. Under the condition of low substrate temperature (45 °C in this experiment) and, therefore, low adatom mobility, the adatom diffusion is too low to fill the voids. Subsequently, isolated long 3D Mg nanostructures along with shorter and tiny Mg nanostructures are formed on the substrate surface, as shown in Figs. 1(a)–1(f).

The structure and composition of the as-prepared 3D Mg nanostructures are identified by XRD and EDX (inset), as shown in Fig. 2. To remove the effect of the well-crystallized single-crystal silicon substrate, Mg nanostructures are manually scratched from the substrate with a sharp knife for XRD and EDX characterizations. The main elements seen in the EDX spectrum are O, Mg, and Si. Si comes from the scratched silicon substrate and O comes from MgO that is formed at the surface of the Mg nanostructures when, taking out of the vacuum deposition chamber, they are let in contact with atmospheric oxygen. However, MgO is not detected by XRD, which is mainly due to its very small thickness at the Mg surface. This is confirmed by the subsequent HRTEM characterization.

Figures 3(a)–3(c) show the electron diffraction patterns of a 3D Mg nanostructure obtained on a JEOL 2010 microscope running at 200 kV indicating a single-crystal structure. They are views of the (011), (021), and (311) reciprocal lattice planes for the hexagonal compact structure of Mg, respectively. The HRTEM image in Fig. 3(d) shows clear fringes with an interplanar spacing of 0.26 nm, which corresponds to the separation between the (002) lattice planes.

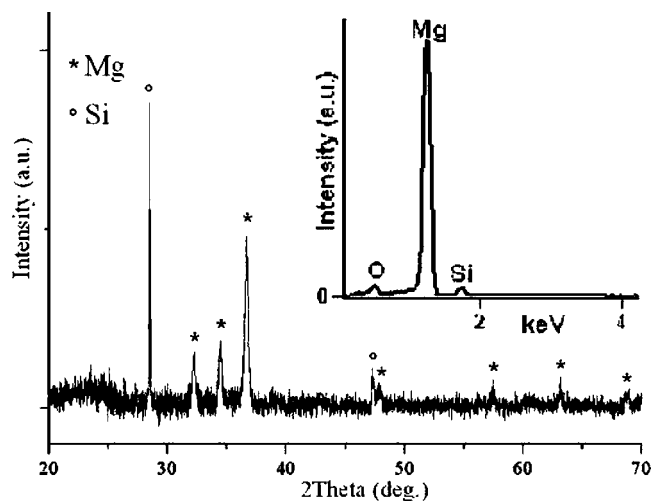


FIG. 2. XRD and EDX patterns of the Mg nanostructures.

These are aligned perpendicular to the longitudinal direction of the 3D prismatic Mg nanostructures, which suggests that the Mg nanostructures grow along the [001] direction. As shown in Fig. 3(d) an ultrathin layer (~2 nm thick) is formed on the surface of Mg after the substrate is taken out of the vacuum chamber and kept for several weeks in air. The interplanar spacing of about 0.21 nm of the ultrathin layer corresponds to the distance between MgO (200) planes. Figure 3(e) is a HRTEM image for a thicker Mg nanostructure compared to that in Fig. 3(d).

The MgO shell prevents further oxidation under ambient conditions. For metal oxide growth, inward diffusion of anions or outward diffusion of cations needs to be balanced by electron transport from the metal-oxide interface to the oxide surface where the adsorbed oxygen is ionized.²⁶ At room temperature, electron transport through the oxide layer is done by tunneling mechanism, which decreases exponentially with the increase in the oxide layer thickness. When the layer thickness arrives to a few nanometers, the oxide growth terminates if there are not other active transport mechanisms. The effect on the hydrogen uptake of magnesium oxide formed on the Mg surface has been addressed before.^{11,27} If the oxide layer is ultrathin, it will increase the hydrogen uptake rate. This is because thin oxides form a “patched” pattern on the surface of bulk Mg and still allow

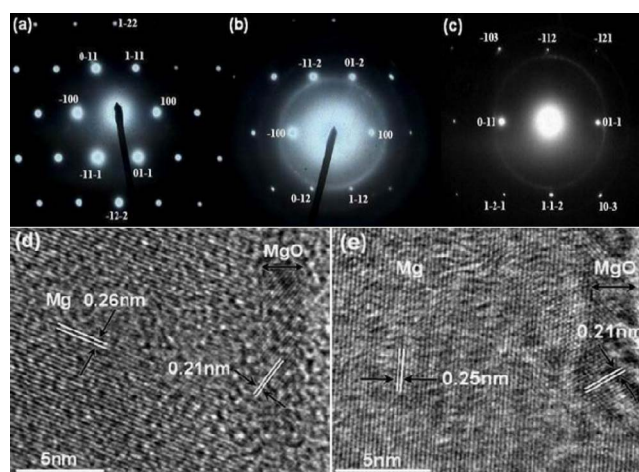


FIG. 3. (Color online) TEM and HRTEM images of the Mg nanostructure.

hydrogen to diffuse into the bulk of Mg. It is also likely that the formation of an ultrathin oxide layer can favor hydrogen diffusion into the bulk of Mg by prohibiting the formation of a “surface shell” of MgH₂ that further frustrates hydrogen diffusion. However, if the oxide layer becomes thick and compact, it will reduce or even totally block the hydrogen uptake.

The as-prepared 3D Mg nanostructures are also characterized by surface area measurement. Mg is deposited onto silicon substrate with a deposition time of 800 s. After deposition, Mg nanostructures are manually scratched from the substrate and placed into an analysis cell for the surface area measurement. The samples (with a mass of 2 mg) are out-gassed under primary vacuum at 250 °C for 3 h. The krypton adsorption isotherms are determined at 77 K, by volumetric method, with a Micromeritics ASAP 2010M device. The isotherms are recorded in the relative pressure range from 0.07 to 0.33. Using the Brunauer–Emmett–Teller method²⁸ and 0.21 nm² as Kr cross section, the specific surface area computed from the isotherms is about 135 m²/g. The large value of the specific surface area is mainly due to the 3D character of the nanostructures. Another cause is the high surface roughness of the 3D nanostructures. As shown in Fig. 1(a), the 3D prislake nanostructures are formed layer by layer but with different layer cross-sectional areas, thus, resulting in high surface roughness.

The approach employed in this study has several merits. First, the fabrication process of the 3D Mg nanostructures is very simple. A conventional thermal evaporator can be directly utilized. Second, uniform 3D Mg nanostructures can be deposited on several silicon wafers simultaneously. Consequently, it is suitable for mass production. Third, the nanostructures are formed by physical self-assembly under a high vacuum and a low substrate temperature, thus, resulting in relatively pure nano-Mg. Fourth, the dimensions of the 3D Mg nanostructures can be tailored by controlling the deposition conditions, for instance, the deposition time. Fifth, the 3D Mg nanostructures are realized onto silicon that is a basic material for microelectronics and microsystem. This will therefore open the door to integrate the nanostructures into microsystem, thus, leading to potential functional nanodevices.

In conclusion, 3D prislake Mg nanostructures have been realized onto silicon substrate by thermal evaporation under an oblique angle. This method has some merits over previous approaches including more suitability for mass production, reduced impurities, and tailored dimensions. SEM observations show that most of the 3D Mg nanostructures are

vertically aligned along the substrate surface. XRD, TEM, and HRTEM characterizations show that the 3D nano-Mg are hexagonal compact single-crystal structures. An ultrathin MgO layer with a thickness of 1.5–2.5 nm is formed at the surface of the Mg nanostructures when they are let in contact with atmospheric oxygen. The measured specific surface area of the 3D nano-Mg is around 135 m²/g.

- ¹Y. N. Xia, P. D. Yang, Y. G. Sun, Y. Y. Wu, B. Mayers, B. Gates, Y. D. Yin, F. Kim, and H. Q. Yan, *Adv. Mater. (Weinheim, Ger.)* **15**, 353 (2003).
- ²C. Burda, X. B. Chen, R. Narayanan, and M. A. El-Sayed, *Chem. Rev. (Washington, D.C.)* **105**, 1025 (2005).
- ³L. Schlapbach and A. Züttel, *Nature (London)* **414**, 353 (2001).
- ⁴W. Grochala and P. P. Edwards, *Chem. Rev. (Washington, D.C.)* **104**, 1283 (2004).
- ⁵X. F. Wang and L. Andrews, *J. Phys. Chem. A* **108**, 11511 (2004).
- ⁶R. W. P. Wagemans, J. H. van Lenthe, P. E. de Jongh, A. J. van Dillen, and K. P. de Jong, *J. Am. Chem. Soc.* **127**, 16675 (2005).
- ⁷D. Aurbach, Z. Lu, A. Schechter, Y. Gofer, H. Gizbar, R. Turgeman, Y. Cohen, M. Moshkovich, and E. Levi, *Nature (London)* **407**, 724 (2000).
- ⁸J. A. Cowan, *The Biological Chemistry of Magnesium* (VCH, New York, 1995).
- ⁹P. Dai, P. H. Dussault, and T. K. Trullinger, *J. Org. Chem.* **69**, 2851 (2004).
- ¹⁰Y. K. Zhang, S. J. Liao, and Y. H. Fan, *J. Nanopart. Res.* **3**, 23 (2001).
- ¹¹B. J. Kooi, G. Palasantzas, and J. T. M. De Hosson, *Appl. Phys. Lett.* **89**, 161914 (2006).
- ¹²E. Shalaan and H. Schmitt, *Surf. Sci.* **600**, 3650 (2006).
- ¹³Z. Dehouche, J. Goyette, T. K. Bose, J. Huot, and R. Schulz, *Nano Lett.* **1**, 175 (2001).
- ¹⁴J. Chen, T. Sakai, N. Kitamura, H. T. Takeshita, and N. Kuriyama, *J. Am. Chem. Soc.* **123**, 6193 (2001).
- ¹⁵J. Huot, J. F. Pelletier, L. B. Lurio, M. Sutton, and R. Schulz, *J. Alloys Compd.* **348**, 319 (2003).
- ¹⁶J. L. Bobet, E. Grigorova, M. Khrussanova, M. Khristov, P. Stefanov, P. Peshev, and D. Radev, *J. Alloys Compd.* **366**, 298 (2004).
- ¹⁷L. Lu, M. O. Lai, and W. Liang, *Compos. Sci. Technol.* **64**, 2009 (2004).
- ¹⁸N. Hanada, T. Ichikawa, and H. Fujii, *J. Phys. Chem. B* **109**, 7188 (2005).
- ¹⁹W. Y. Li, C. S. Li, C. Y. Zhou, H. Ma, and J. Chen, *Angew. Chem., Int. Ed.* **45**, 6009 (2006).
- ²⁰W. Y. Li, C. S. Li, H. Ma, and J. Chen, *J. Am. Chem. Soc.* **129**, 6710 (2007).
- ²¹Z. L. Wang and Z. W. Pan, *Adv. Mater. (Weinheim, Ger.)* **14**, 1029 (2002).
- ²²T. Yu, Y. Zhu, X. Xu, Z. Shen, P. Chen, C. T. Lim, J. T. L. Thong, and C. H. Sow, *Adv. Mater. (Weinheim, Ger.)* **17**, 1595 (2005).
- ²³S. Park, J. H. Lim, S. W. Chung, and C. A. Mirkin, *Science* **303**, 348 (2004).
- ²⁴L. S. Zhong, J. S. Hu, H. P. Liang, A. M. Cao, W. G. Song, and L. J. Wan, *Adv. Mater. (Weinheim, Ger.)* **18**, 2426 (2006).
- ²⁵K. Robbie, M. J. Brett, and A. Lakhtakia, *Nature (London)* **384**, 616 (1996).
- ²⁶A. T. Fromhold, Jr. and E. L. Cook, *Phys. Rev.* **158**, 600 (1967).
- ²⁷P. Hjort, A. Krozer, and B. Kasemo, *J. Alloys Compd.* **237**, 74 (1996).
- ²⁸S. Brunauer, P. H. Emmett, and E. Teller, *J. Am. Chem. Soc.* **60**, 309 (1938).