



HAL
open science

Realization of aligned three-dimensional single-crystal chromium nanostructures by thermal evaporation

Kaili Zhang, Christophe Tenaillau, Pierre Alphonse, Jean-Yves Chane-Ching

► To cite this version:

Kaili Zhang, Christophe Tenaillau, Pierre Alphonse, Jean-Yves Chane-Ching. Realization of aligned three-dimensional single-crystal chromium nanostructures by thermal evaporation. Applied physics. A, Materials science & processing, 2010, 100 (4), pp.1049-1055. <10.1007/s00339-010-5905-8>. <hal-03550361>

HAL Id: hal-03550361

<https://hal.science/hal-03550361v1>

Submitted on 1 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.



HAL Authorization



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 : 4748

To link to this article : DOI :10.1007/s00339-010-5905-8
URL : <http://dx.doi.org/10.1007/s00339-010-5905-8>

To cite this version : Zhang, Kaili and Tenailleau, Christophe and Alphonse, Pierre and Chane-Ching, Jean-Yves (2010) *Realization of aligned three-dimensional single-crystal chromium nanostructures by thermal evaporation*. Applied Physics A: Materials Science & Processing, vol. 100 (n° 4). pp. 1049-1055. ISSN 0947-8396

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

Realization of aligned three-dimensional single-crystal chromium nanostructures by thermal evaporation

Kaili Zhang · Christophe Tenailleau · Pierre Alphonse · Jean-Yves Chane-Ching

Abstract Aligned three-dimensional single-crystal chromium nanostructures are fabricated onto a silicon substrate by thermal evaporation in a conventional thermal evaporator, where the incident angle of Cr vapor flux with respect to the substrate surface normal is fixed at 88° . The effects of the deposition time and incident angle on the morphology of the resulting nanostructures are investigated. The achieved Cr nanostructures are characterized by scanning electron microscopy, energy dispersive X-ray analysis, X-ray diffraction, transmission electron microscopy, high-resolution transmission electron microscopy, and surface area measurement. This study provides a convenient way to fabricate three-dimensional single-crystal Cr nanostructures, which is suitable for batch fabrication and mass production. Finally, the same technique is employed to fabricate the nanostructures of other metals such as Ag, Au, Pd, and Ni.

1 Introduction

Nanoscale metals are being extensively investigated because of their promising applications and improved properties compared to their bulk or micro counterparts [1, 2]. Chromium, an interesting transition metal, has found various applications in many fields including metallurgy, catalysis, magnetic field, and semiconductors [3–10]. For instance,

K. Zhang (✉)
Department of Manufacturing Engineering and Engineering Management, City University of Hong Kong, 83 Tat Chee Avenue, Hong Kong, Hong Kong
e-mail: kaizhang@cityu.edu.hk
e-mail: kaili_zhang@hotmail.com
Fax: +852-34420172

C. Tenailleau · P. Alphonse · J.-Y. Chane-Ching
CIRIMAT, Université Paul Sabatier, 118 route de Narbonne, 31062 Toulouse, France

Cr is a commercially available transition metal that adheres well to silicon substrates, which makes Cr being widely used in silicon based semiconductors both in research and in industry. Cr thin films [5–7] and nanoparticles [8–10] have been intensively studied, and improved catalytic and magnetic performances have been found compared to those for bulk Cr. Although Cr thin films and nanoparticles have been extensively investigated, there are very few studies on two-dimensional (2D) and three-dimensional (3D) Cr nanostructures. It is widely accepted that 2D/3D nanostructures are important components for nanoscale devices with many promising applications, due to their large surface areas and other unique properties [11–15]. Consequently, it will be very interesting to synthesize 2D/3D Cr nanostructures.

In this work, a convenient way is presented to synthesize aligned 3D single-crystal Cr nanostructures onto a silicon substrate using thermal evaporation in a conventional thermal evaporator. The experimental processes are first described. The effects of the deposition time and incident angle on the morphology of the resulting nanostructures are studied by scanning electron microscopy (SEM). The synthesized 3D Cr nanostructures are also characterized by energy dispersive X-ray analysis (EDX), X-ray diffraction (XRD), transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), and surface area measurement. The same technique is employed to realize other metal nanostructures as well.

2 Experiment

The 3D nanostructures of Cr are synthesized by a VEECO 770 thermal evaporating system using 99.99% pure Cr pellets as the source material. An alumina crucible is used as the source holder, and a tungsten filament is employed to

thermally heat the source holder. Half of a 4-inch p-type single-crystal silicon wafer is used as the substrate that is cleaned using acetone, chromic sulfuric acid mixture, thoroughly rinsed by deionized water and blow dried by nitrogen. Then the silicon substrate is put into an oven for further drying at 200°C for 20 min. The silicon substrate is mounted into a specific movable holder inside the evaporation chamber. The incident angle of Cr vapor flux with respect to the silicon substrate surface normal is fixed at 88°. The distance between the top of the substrate and the source holder is around 18 cm. The Cr is evaporated with a constant supply current of 23 A and a vacuum level of 7×10^{-6} mbar. The deposition rate is set to be 5 Å/s, and the temperature of the substrate is about 45°C during the thermal evaporation. The deposited Cr nanostructures on the substrate are directly characterized by SEM and EDX. For XRD characterization, the Cr nanostructures are scratched from the substrate to avoid the effect of the well-crystallized silicon substrate. XRD patterns are recorded on a Bruker D4-Endeavor diffractometer using Cu K α radiation (40 kV, 40 mA) from 20 to 100° in 2-Theta with a 0.016° step scan, a real-time/step of 0.13 s on a linear Bruker LynxEye detector, and 30 rotation/min. For TEM and HRTEM characterizations, the Cr nanostructures are manually scratched from the silicon substrate, mixed with ethanol, and deposited onto carbon-coated copper grids. TEM images and electron dif-

fraction patterns are obtained on a JEOL 2010 microscope running at 200 kV. HRTEM images are taken with a JEOL 2100F microscope operating at 200 kV.

3 Results

3.1 SEM characterization

Figure 1(a) is a top view SEM image of the Cr nanostructures, and the deposition time is set as 400 s. Most of the Cr nanostructures become bigger and bigger as they grow from the substrate surface. Figures 1(b) and (c) are cross-section view SEM images of the Cr nanostructures taken at different directions. The length of the larger Cr nanostructures is around 0.2 μm . However, besides the larger ones, smaller and shorter structures can be seen from Figs. 1(a)–(c). Figure 1(d) shows a 45° tilted view SEM image. Roughly, the top surface of most of the Cr nanostructures is crescent-shaped. Figures 1(a)–(d) confirm the 3D structure of the realized nano Cr. Experiments show that relatively homogeneous Cr nanostructures can be formed on the entire surface of the half of a 4-inch silicon wafer. Therefore, the approach is suitable for batch fabrication and mass production.

It is possible to tailor the dimensions of the Cr nanostructures by controlling the deposition conditions. For example,

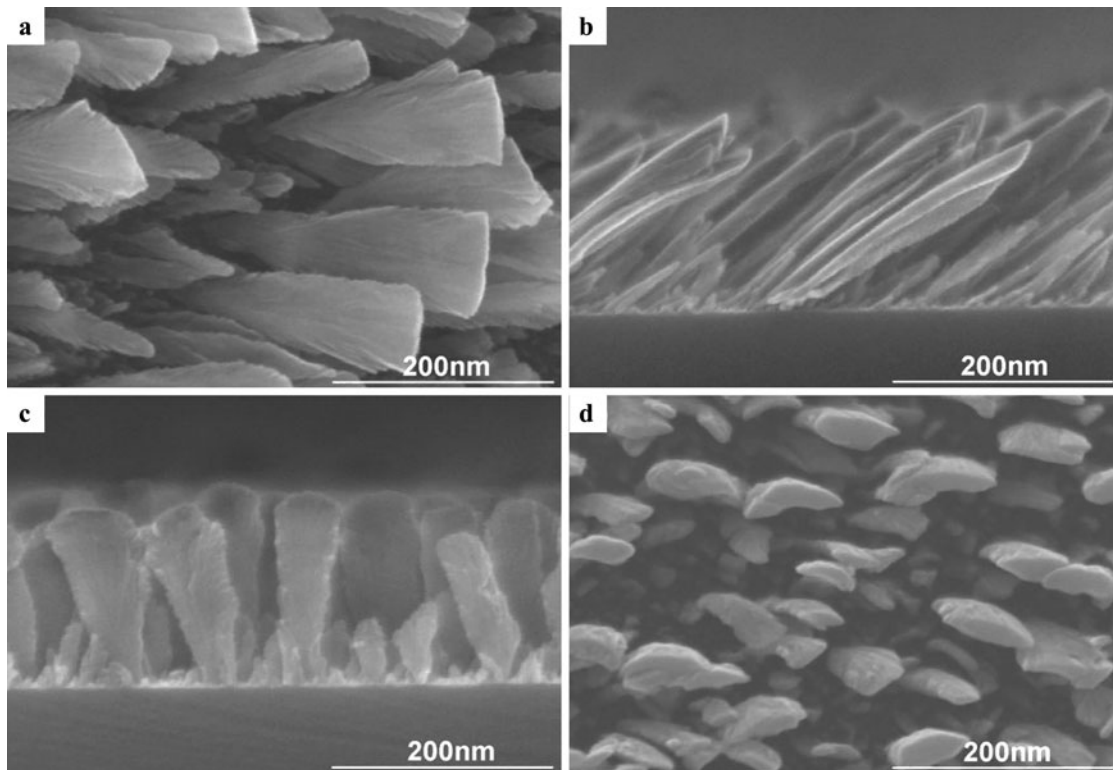


Fig. 1 SEM images of the as-prepared 3D Cr nanostructures with a deposition time of 400 s: (a) top view, (b) cross-section view, (c) cross-section view, and (d) 45° tilted view

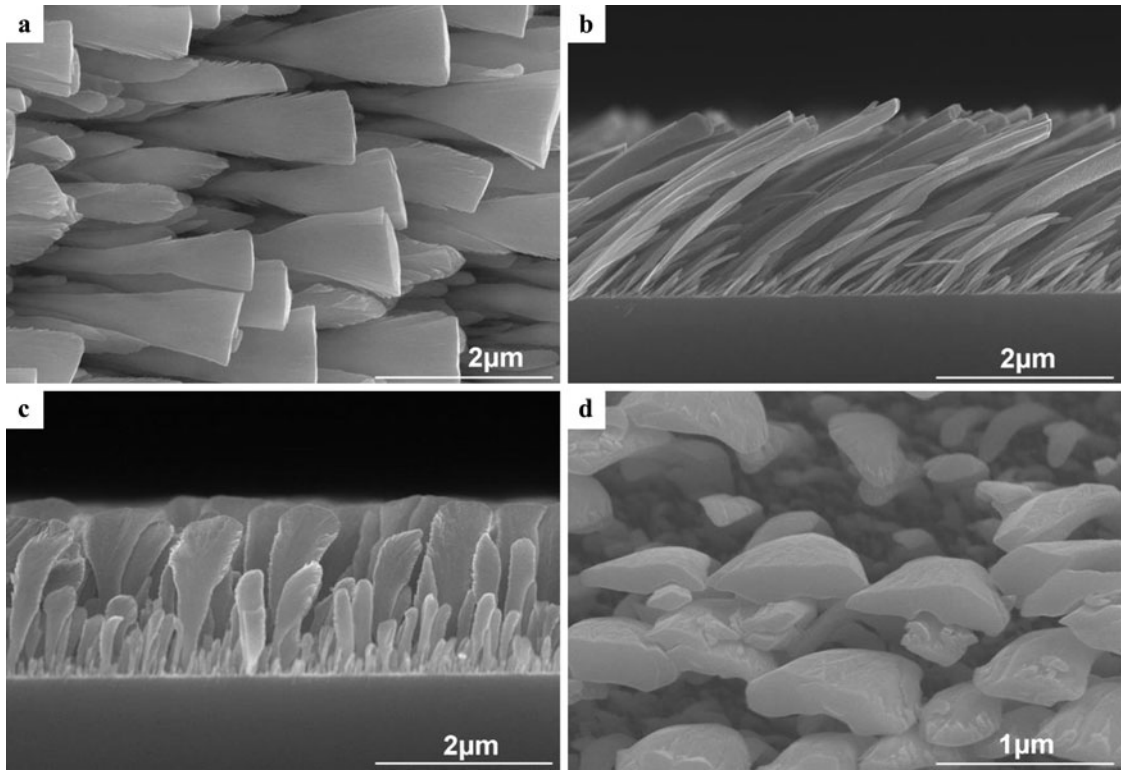


Fig. 2 SEM images of the as-prepared 3D Cr nanostructures with a deposition time of 4000 s: (a) top view, (b) cross-section view, (c) cross-section view, and (d) 45° tilted view

Fig. 2(a) shows a top view SEM image of the Cr nanostructures with a deposition time of 4000 s. Figures 2(b) and (c) are the cross-section view SEM images that are taken at different directions. The resulting length of the Cr nanostructures is about 2 μm . Figure 2(d) is a 45° tilted view SEM image of the Cr nanostructures. The dimensions are significantly increased although the 45° tilted view surface keeps a similar shape (crescent) as that for Cr nanostructures with a deposition time of 400 s.

The incident angle of the Cr vapor flux with respect to the substrate surface normal can also greatly affect the resulting morphology of the Cr nanostructures. Figure 3(a) is a SEM image of the deposited Cr structure with a deposition time of 400 s at an incident angle of 0°, where dense Cr thin film is formed. When the incident angle is increased from 60° to 80°, 3D Cr nanostructures start to form as shown in Figs. 3(b) and (c), respectively. Atomic shadowing and adatom diffusion are the two dominant mechanisms that control the growth of the 3D Cr nanostructures [16]. At the early stage of the deposition by thermal evaporation, the initial Cr nuclei are first formed on the silicon substrate surface. These nuclei prevent the subsequent Cr vapor flux from reaching directly some areas of the substrate surface because of the atomic shadowing at high incident angles with respect to the substrate surface normal. If the substrate temperature is low (45°C in this study), adatom mobility is also low. The

adatom diffusion cannot fill the voids due to the low adatom mobility. As a result, isolated long 3D Cr nanostructures, together with shorter and small Cr nanostructures, are formed on the silicon substrate surface as can be seen from Figs. 1 and 2.

3.2 EDX and XRD characterizations

The as-prepared 3D nanostructures on silicon substrate are directly characterized by EDX as shown in Fig. 4. The main elements seen in the spectrum are Cr and Si, where Si comes from the silicon substrate. O is not detected by EDX indicating that the Cr nanostructures are not oxidized when, taken out of the vacuum deposition chamber, they are let in contact with atmospheric oxygen. To try to minimize the effect of the silicon substrate, Cr nanostructures are manually scratched from the substrate for XRD characterization as shown in Fig. 5. The peaks for Cr are clearly seen on the XRD pattern. There are still peaks for Si resulted from the scratched well-crystallized single-crystal silicon.

3.3 TEM and HRTEM characterizations

Figure 6(a) is a TEM image for the scratched 3D Cr nanostructures with a deposition time of 400 s. There are many

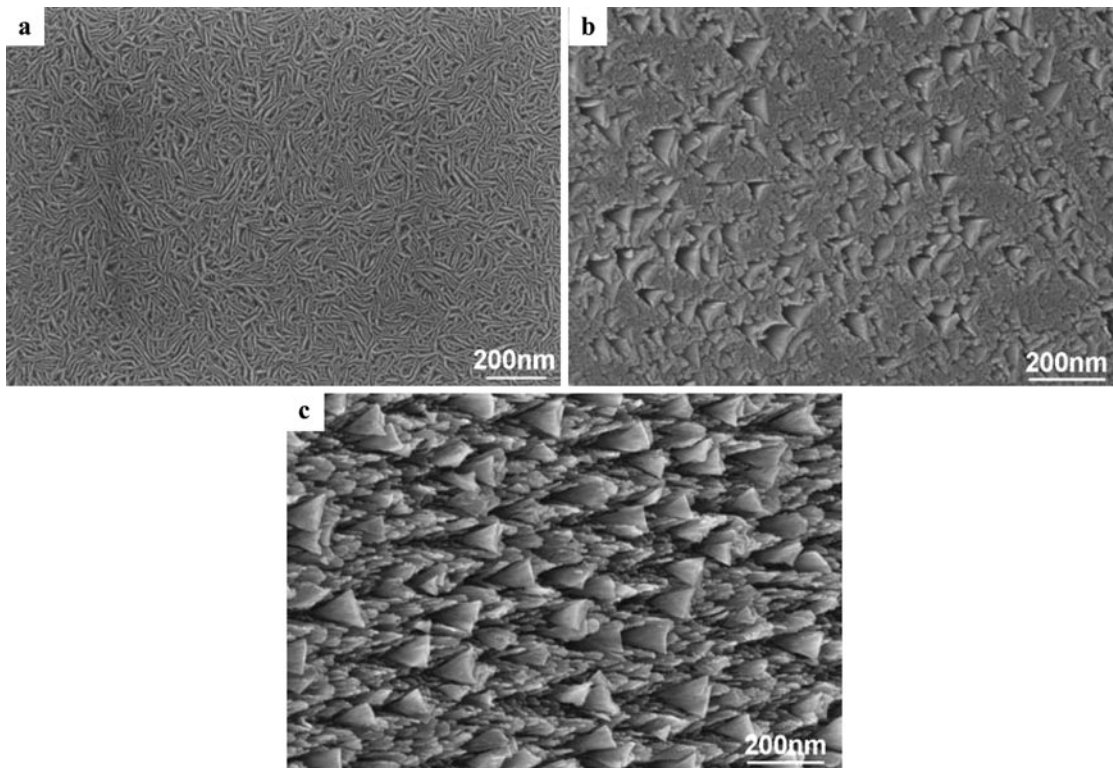
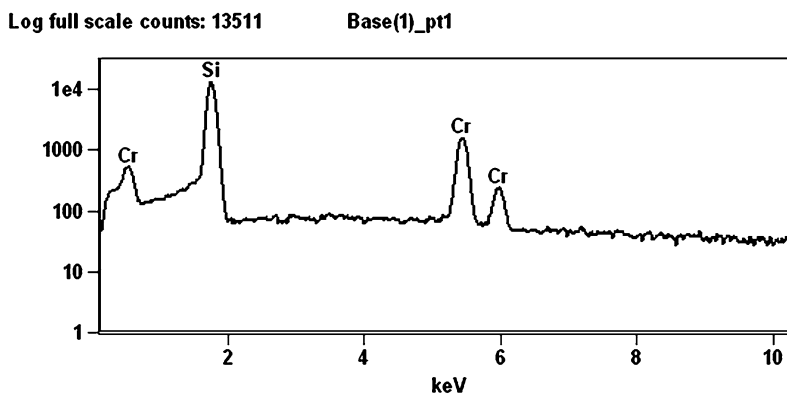


Fig. 3 SEM images of the deposited Cr film and nanostructures with a deposition time of 400 s at different incident angles: (a) 0°, (b) 60°, and (c) 80°

Fig. 4 EDX pattern of the Cr nanostructures



protruding tiny structures at the edges of the 3D Cr nanostructures. Figure 6(b) shows an electron diffraction pattern of a 3D Cr nanostructure obtained on a JEOL 2010 microscope running at 200 kV, which indicates a single-crystal structure. It is a view of the slightly tilted (111) reciprocal lattice plane for bcc chromium. Figures 7(a) and (b) are two HRTEM images for the Cr nanostructures showing clear fringes with an interplanar spacing of 0.18 nm that corresponds to the separation between the (110) lattice planes.

3.4 BET surface area measurement

Surface area measurement is also used to characterize the 3D Cr nanostructures. About 5 mg of Cr nanostructures with

a deposition time of 4000 s are manually scratched from the substrate and put into an analysis cell for the measurement. The samples are outgassed under primary vacuum at 250°C for 3 h. The Krypton adsorption isotherms are recorded at 77 K using a Micromeritics ASAP 2010M device in the relative pressure range from 0.07 to 0.33. Employing the BET method [17] and 0.21 nm² as Kr cross section, the specific surface area of the 3D Cr nanostructures computed from the isotherms is around 11 m²/g.

3.5 Deposition of other metal nanostructures

This technique had been used to synthesize 3D prism-like nanostructures of Mg as described in [15]. After that work,

Fig. 5 XRD pattern of the Cr nanostructures

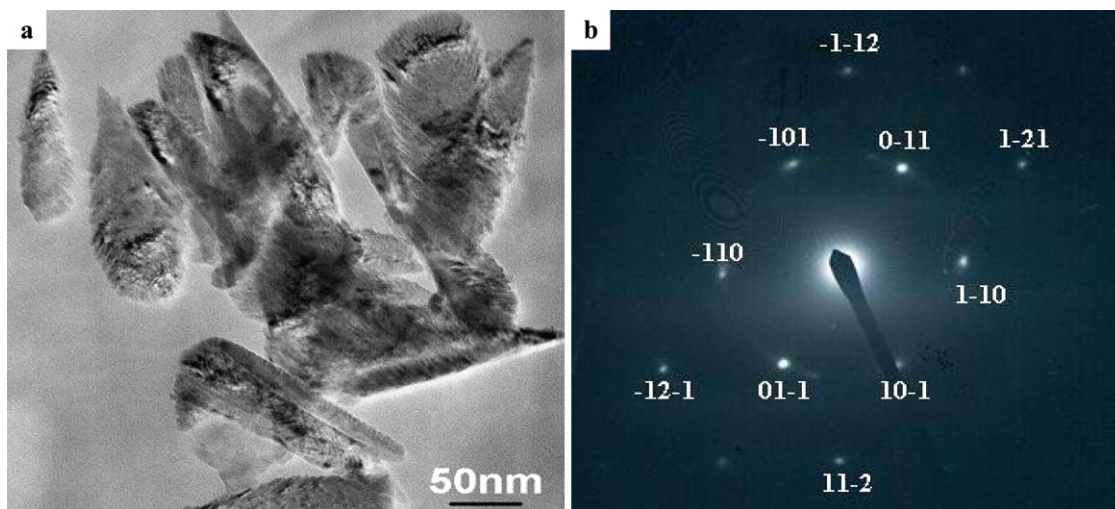
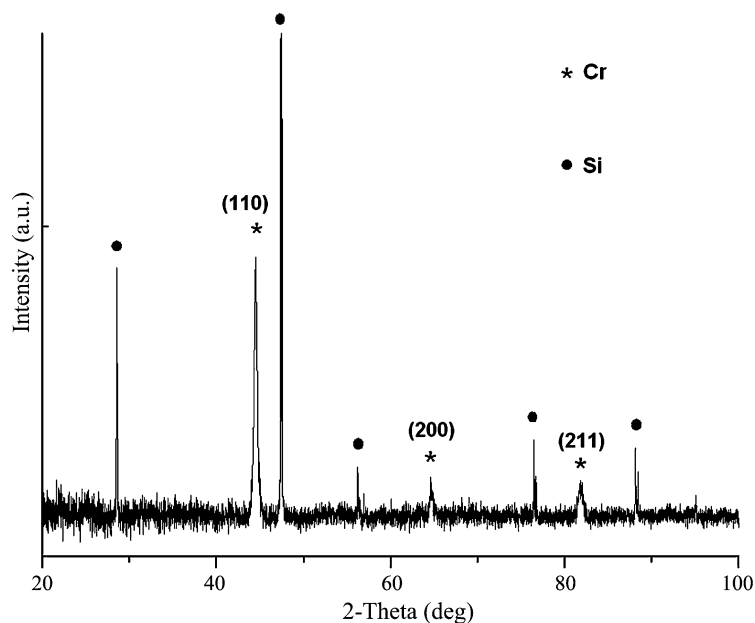


Fig. 6 TEM image and electron diffraction pattern of the Cr nanostructures with a deposition time of 400 s

different metals including Ag, Au, AuSb, Cr, Ge, Ni, NiCr, NiFe, Pd, Pt, and Ti have been deposited by thermal evaporation in a conventional thermal evaporator, where the incident angle of the metal vapor flux with respect to the substrate surface normal is fixed at 88° . The 3D nanostructure is achieved only with Cr as reported in this study. The deposited nanostructures of other metals are basically nanorods as shown in Figs. 8(a) to (d), and many of them are not well separated from each other as can be seen from Figs. 8(b) to (d).

The method used in this study to synthesize 3D single-crystal Cr nanostructures has several advantages including simple fabrication process utilizing commercially available conventional thermal evaporators, suitable for batch fabri-

cation and mass production, realization of pure Cr nanostructures, and tailored dimensions of the deposited nanostructures on a semiconducting silicon substrate. The synthesized 3D Cr nanostructures in this work have many potential applications. For instance, optical angular selectivity is a promising property to achieve energy efficiency, good day lighting, and comfort with sloping windows in buildings/cars. Optical angular selectivity could be obtained in the 3D Cr nanostructures because they may contain inclined absorbing regions of sizes smaller than the wavelength of visible light. Therefore, the 3D Cr nanostructures are promising materials for window coatings to improve energy efficiency in buildings/cars.

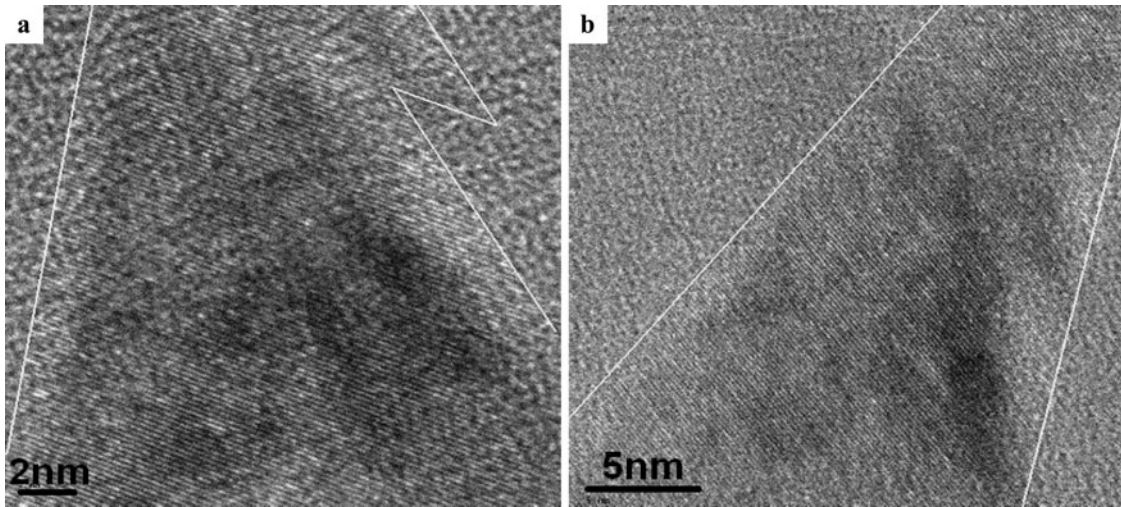


Fig. 7 HRTEM images of the Cr nanostructures

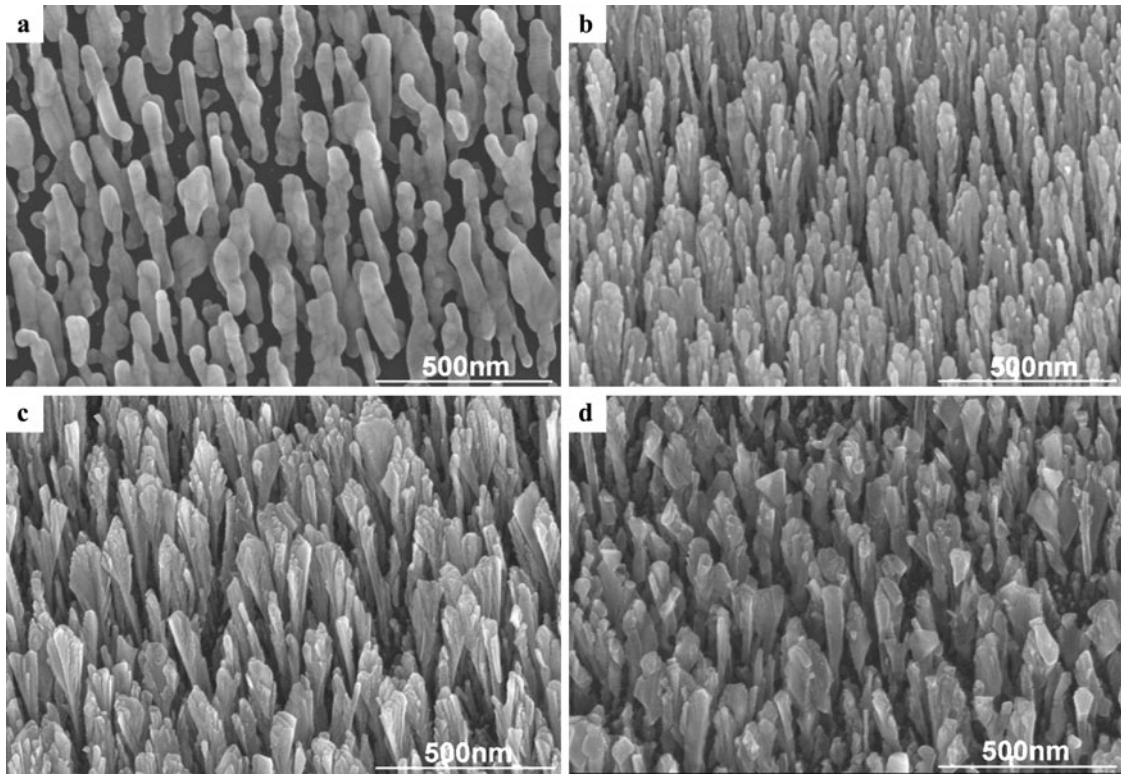


Fig. 8 SEM images of the deposited metals with an incident angle of 88° : (a) Ag, (b) Au, (c) Pd, and (d) Ni

4 Conclusion

Aligned three-dimensional single-crystal chromium nanostructures have been fabricated onto a silicon substrate by thermal evaporation in a conventional thermal evaporator under an oblique angle. The deposition time and incident angle can have great effects on the morphology of the resulting nanostructures. SEM images show that most of the

3D Cr nanostructures are well aligned along the silicon substrate surface. EDX and XRD characterizations confirm that the realized nanostructures are pure Cr. XRD, TEM, and HRTEM characterizations show that the as-prepared 3D Cr nanostructures are single-crystal. The synthesis method used in this study has several merits such as suitable for batch fabrication and mass production, reduced impurities, and tailored dimensions of the resulting Cr nanostructures. Since

the 3D Cr nanostructures are realized onto silicon, a basic material for microelectronics and microsystem, this will probably open the door to integrate the 3D Cr nanostructures into microsystem, thus leading to functional nanodevices.

References

1. Y.N. Xia, P.D. Yang, Y.G. Sun, Y.Y. Wu, B. Mayers, B. Gates, Y.D. Yin, F. Kim, H.Q. Yan, One-dimensional nanostructures: synthesis, characterization, and applications. *Adv. Mater.* **15**(5), 353–389 (2003)
2. C. Burda, X.B. Chen, R. Narayanan, M.A. El-Sayed, Chemistry and properties of nanocrystals of different shapes. *Chem. Rev.* **105**, 1025–1102 (2005)
3. M.J. Udy, *Chromium: Metallurgy of Chromium and Its Alloys*, vol. II (Reinhold, New York, 1956)
4. J.F. Lawler, R.G.P. van der Kraan, H. van Kempen, A.J. Quinn, Growth of Cr on Cu (001) studied by scanning tunneling microscopy. *Phys. Rev. B* **53**(16), 11159–11163 (1996)
5. G.W. Mbise, D.L. Bellac, G.A. Niklasson, C.G. Granqvist, Angular selective window coatings: theory and experiments. *J. Phys. D, Appl. Phys.* **30**, 2103–2122 (1997)
6. D. Qian, G.L. Liu, D. Loison, G.S. Dong, X.F. Jin, Growth and structure of Cr thin films on GaAs(001). *J. Cryst. Growth* **218**, 197–202 (2000)
7. C. Kaito, H. Nakamura, S. Kimura, Y. Kimura, T. Nakada, Y. Saito, The structure of thin Cr film prepared by the vacuum evaporation method. *Thin Solid Films* **359**, 283–287 (2000)
8. R.D. Tilley, D.A. Jefferson, The preparation of chromium, nickel and chromium-nickel alloy nanoparticles on supports. *J. Mater. Chem.* **12**, 3809–3813 (2002)
9. S.U. Son, Y. Jang, K.Y. Yoon, C. An, Y. Hwang, J.G. Park, H.J. Noh, J.Y. Kim, J.H. Park, T. Hyeon, Synthesis of monodisperse chromium nanoparticles from the thermolysis of a Fischer carbene complex. *Chem. Commun.* **1**, 86–88 (2005)
10. W.S. Zhang, E. Bruck, Z.D. Zhang, O. Tegus, W.F. Li, P.Z. Si, D.Y. Geng, K.H.J. Buschow, Structure and magnetic properties of Cr nanoparticles and Cr₂O₃ nanoparticles. *Physica B* **358**, 332–338 (2005)
11. Z.L. Wang, Z.W. Pan, Junctions and networks of SnO nanoribbons. *Adv. Mater.* **14**(15), 1029–1032 (2002)
12. T. Yu, Y. Zhu, X. Xu, Z. Shen, P. Chen, C.T. Lim, J.T.L. Thong, C.H. Sow, Controlled growth and field-emission properties of cobalt oxide nanowalls. *Adv. Mater.* **17**(13), 1595–1599 (2005)
13. S. Park, J.H. Lim, S.W. Chung, C.A. Mirkin, Self-assembly of mesoscopic metal-polymer amphiphiles. *Science* **303**, 348–351 (2004)
14. L.S. Zhong, J.S. Hu, H.P. Liang, A.M. Cao, W.G. Song, L.J. Wan, Self-assembled 3D flowerlike iron oxide nanostructures and their application in water treatment. *Adv. Mater.* **18**, 2426–2431 (2006)
15. K. Zhang, C. Rossi, C. Tenailleau, P. Alphonse, Aligned three-dimensional prism-like magnesium nanostructures realized onto silicon substrate. *Appl. Phys. Lett.* **92**(6), 063123 (2008)
16. K. Robbie, M.J. Brett, A. Lakhtakia, Chiral sculptured thin films. *Nature* **384**, 616 (1996)
17. S. Brunauer, P.H. Emmett, E. Teller, Adsorption of gases in multimolecular layers. *J. Am. Chem. Soc.* **60**, 309–319 (1938)