

## Formation of nanorod-like structures through the thermal annealing of Cr films

HYOUN WOO KIM\*, JU HYUN MYUNG, CHONGMU LEE

School of Materials Science and Engineering, Inha University, Yong Hyun Dong, Nam Gu, Incheon, 402-751, Republic of Korea  
E-mail: hwkim@inha.ac.kr

Published online: 10 March 2006

Chromium (Cr) has superior electrical and magnetic properties, and has attracted a great deal of attention on account of its fundamental growth and potential applications. In addition, Cr is a commercially available transition metal that adheres well to silicon (Si) wafers, which will have potential future applications. Therefore, it is very important to examine the effects of thermal annealing not only for scientific interest but also for practical applications. While materials can be obtained in the nanometer length scale with various geometries, one-dimensional (1D) growth has attracted special attention because the anisotropy in the quantum confinement potentials can be used to produce unusual optical, magnetic, and electronic properties [1, 2]. In order to obtain nanowires or nanorods of the desired materials, many methods have been used for the preparation of 1D nanostructured materials, such as laser ablation [3], template [4], solution [5], arc discharge [6], chemical vapor deposition [7], and other methods [8, 9]. It has been and still is a challenge to find a novel and simple synthetic route for 1D nanosized materials and thermal annealing can be a candidate. This method requires neither complex apparatus and sophisticated technique nor metal catalysts and/or templates as usually needed in other methods.

Several researchers have reported the growth of 1D nanostructures by the simple thermal annealing of films or plates such as silicon carbide thin films [10], C-Ni-In mixture thin films [11], Bi-Sr-Ca-Al-O plates [12] and copper grids [13]. This paper presents the report on the appearance of rod-shaped nanostructures via the thermal annealing of Cr films. Although there have been many reports on the preparation of Cr thin films [14–17] and nanoparticles [18, 19], to the best of our knowledge, nearly no report on the synthesis of Cr 1D structures such as nanorods or nanowires has been published.

A *p*-type (100) Si substrate was cleaned in acetone and rinsed in de-ionized water. Deposition was carried out by RF magnetron sputtering of a Cr target at 300 W at a frequency of 13.56 MHz in a atmosphere containing 20 sccm of argon (Ar) (99.99% purity). The Cr film was grown at

temperature and pressure of 25 °C and  $2.0 \times 10^{-2}$  Torr, respectively. After deposition, the Cr films were annealed in a quartz tube furnace reactor at temperatures ranging from 500–1000 °C in an Ar ambient for 1 hr. The structural characteristics of the films were analyzed by scanning electron microscopy (SEM, Hitachi S-4200) and glancing angle X-ray diffraction (XRD, Philips, CM20T, 200 kV) with an incident angle of 0.5 ° with the detector being rotated to scan the samples, using CuK $\alpha_1$  radiation ( $\lambda = 0.154056$  nm). An energy dispersive X-ray (EDX) spectroscope attached to the SEM was used to determine the chemical composition of the as-prepared products.

Fig. 1a shows the XRD patterns of the as-deposited Cr thin film on Si substrate. The (110) and (200) diffraction peaks can be readily indexed to the cubic structure of Cr with lattice constants of  $a = 2.884$  Å (JCPDS File No. 06-0694). Fig. 1b shows the XRD patterns recorded from the Cr thin film annealed at 500 °C. In addition to the (110) and (200) for Cr, the (110) and (116) peaks diffraction peaks for rhombohedral Cr<sub>2</sub>O<sub>3</sub> (JCPDS 06-0504) can also be found, indicating that a considerable amount of Cr has been oxidized. Fig. 1c shows the XRD patterns of the Cr thin film annealed at 750 °C, showing that the 750 °C-annealed films are no longer single- or poly-crystalline. Further investigation will be needed to determine the associated mechanisms.

Figs 2a and b show the cross-sectional SEM images of the as-deposited and 750 °C-annealed Cr films, respectively. The columnar-like morphology shown in the as-deposited films was not observed in the 750 °C-annealed films. The film thickness of the as-deposited and 750 °C-annealed Cr films, respectively, were approximately 360 nm and 500 nm, showing that the film thickness increases significantly as a result of thermal annealing at 750 °C. Fig. 2b clearly indicates the formation of rodlike nanostructures over the Cr film surfaces. Most of the nanorods were straight. The diameters of the nanorods varied between 60 and 100 nm and the length of some of them was  $>1$  μm.

\* Author to whom all correspondence should be addressed.

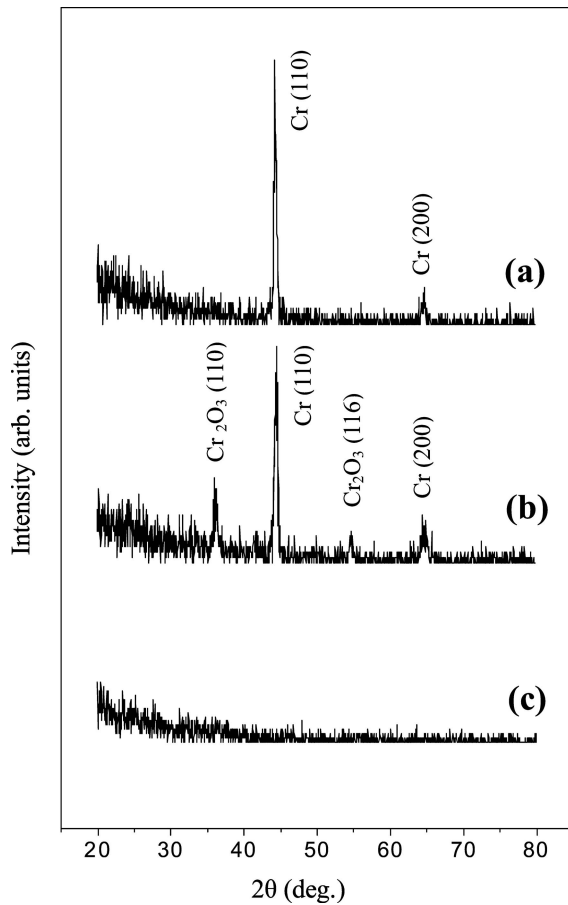


Figure 1 Glancing-angle X-ray diffraction patterns of the Cr thin films (a) as-deposited and after annealing (b) at 500 °C and (c) at 750 °C.

Figs 3a and b show the plan-view SEM images of the Cr films as-deposited and after annealing at 750 °C, respectively. While the grain-like structures of the film surface could be clearly seen in the as-deposited samples, several 1D nanostructures were observed on the surface of 750 °C-annealed sample. Figs 3c and d show the EDX spectrum corresponding to the regions indicated by arrows 1 and 2 in Fig. 3b, respectively. EDX analysis demonstrated that the elements are composed of Si, Cr, and O. It is believed that the Si-related peak is from the underlying substrate. A comparison of the EDX spectra (Figs 3c and d) revealed the nanorods to have a slightly higher Cr/O atomic ratio.

The cross-sectional SEM image shows the volume expansion that occurred during the thermal annealing. The Pilling-Bedworth ratio (PBR, the volume of the oxide divided by that of the metal from which it is formed) of Cr is known to be 2.07 [20] and it is possible that the volume expansion is mainly due to the oxidation of the Cr films. The increase in volume may induce internal stress. Although the driving force is unclear, the internal strain might affect the formation of the nanorod. A similar mechanism was previously reported for the growth of Bi-based alloy whiskers [12]. The plateau-like surface morphology of chromium oxide has been observed with Cr films produced by laser oxidation [20]. In addition, the

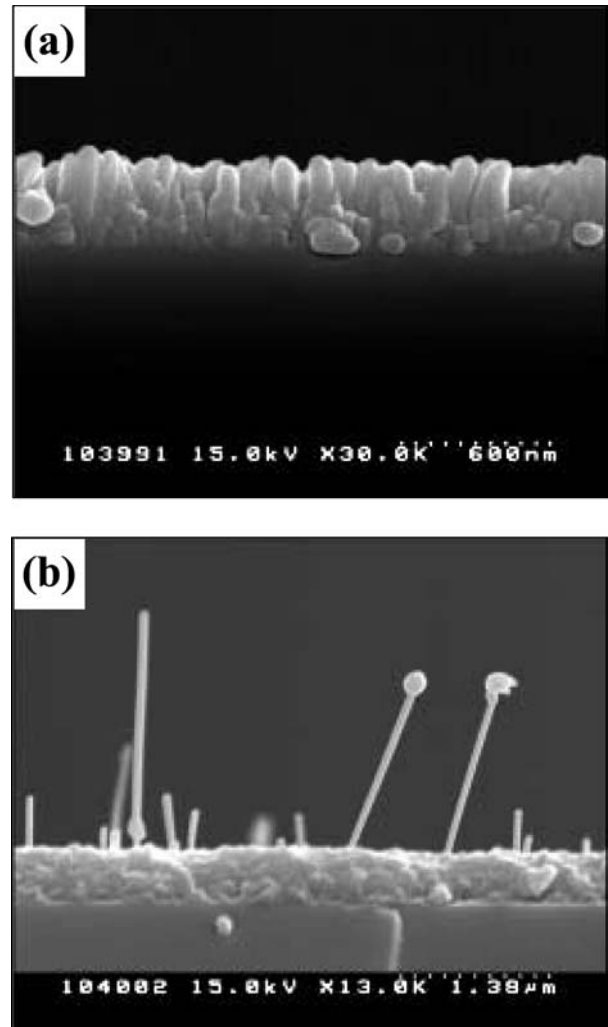


Figure 2 Side-view SEM images of the Cr thin films (a) as-deposited and (b) after annealing at 750 °C.

growth of Cr clusters [21] and nano-scale lines [22] have been demonstrated. However, our extensive literature survey revealed that the growth of nanorod-like structures using thermal annealing or the heating of Cr films had not been reported. Efforts are underway to pursue these routes in more detail to reveal the detailed formation mechanism and crystalline nature of the nanorods.

In summary, this study investigated the effects of thermal annealing on the structural properties of Cr films deposited on Si substrates. With the thermal annealing at 750 °C, unusual 1D nanometer-scale structures were formed on the surface of the films. These nanorods had a circular cross section with diameters ranging from 60–100 nm. The ability to process Cr into nanostructured materials will enhance its performance in future industrial applications and enrich our understanding of its fundamental properties.

#### Acknowledgment

This work was supported by INHA UNIVERSITY Research Grant.

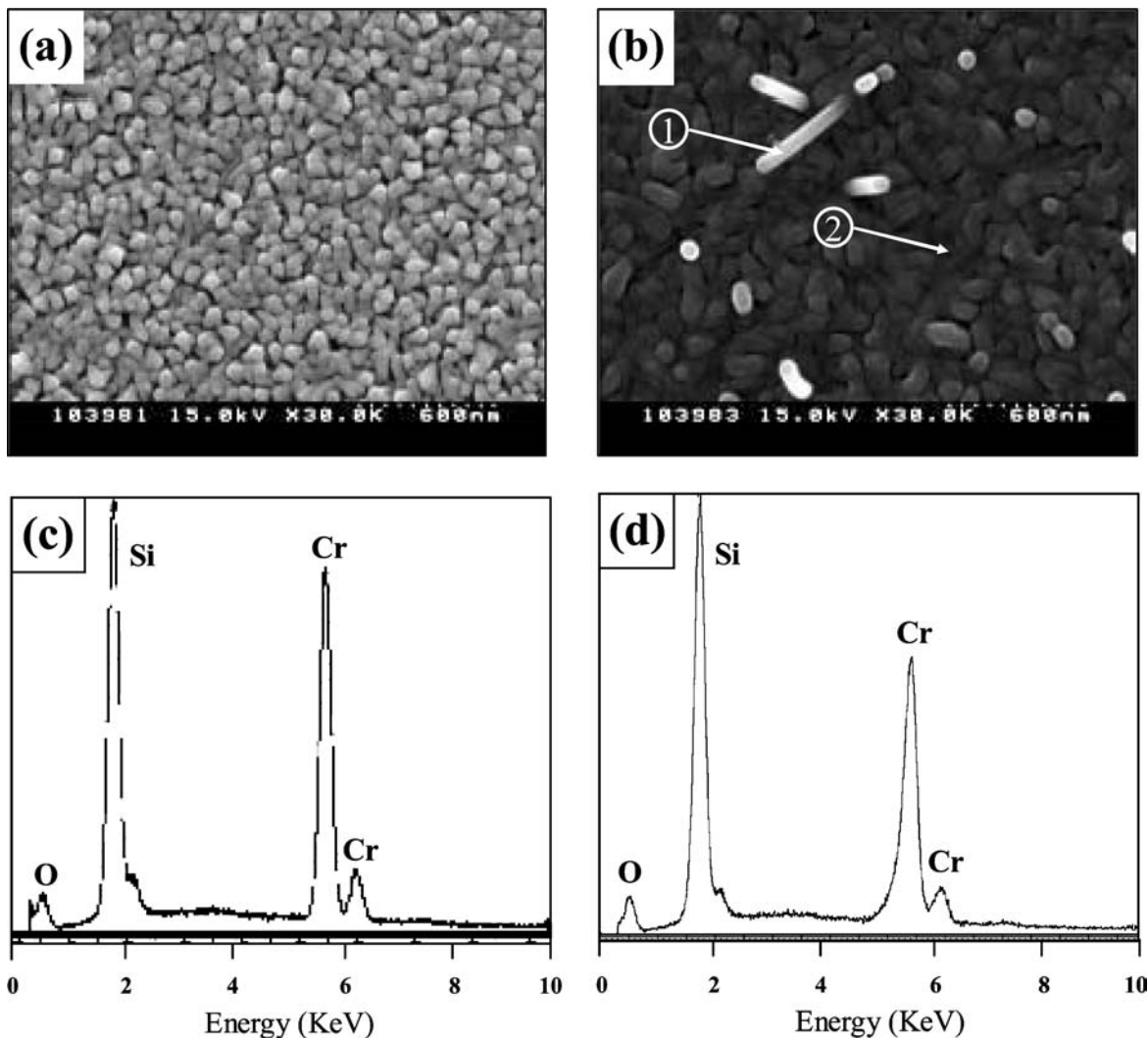


Figure 3 Top-view SEM images of Cr thin films (a) as-deposited and (b) after annealing at 750 °C. (c, d) EDX spectra from the regions indicated by (c) arrow 1 and (d) arrow 2 in Fig. 3b.

## References

1. J. HU, T. W. ODOM and C. M. LIEBER, *Acc. Chem. Res.* **32** (1999) 435.
2. Y. CUI and C. M. LIEBER, *Science* **291** (2001) 851.
3. A. M. MORALES and C. M. LIEBER, *ibid.* **279** (1998) 208.
4. C. R. MARTIN, *ibid.* **266** (1994) 1961.
5. Y. LI, Y. DING and Z. WANG, *Adv. Mater.* **11** (1999) 847.
6. Y. C. CHOI, W. S. KIM, Y. S. PARK, S. M. LEE, D. J. BAE, Y. H. LEE, G.-S. PARK, W. B. CHOI, N. S. LEE and J. M. KIM, *ibid.* **12** (2000) 746.
7. X. CHEN, J. XU, R. M. WANG and D. YU, *ibid.* **15** (2003) 419.
8. Z. W. PAN, Z. R. DAI and Z. L. WANG, *Science* **291** (2001) 1947.
9. Z. G. BAI, H. Z. ZHANG, Y. DING, Y. P. WANG, X. Z. GAI, Q. L. HANG, G. C. XIANG and S. Q. FENG, *Chem. Phys. Lett.* **303** (1999) 311.
10. A. XIA, Z. HUIZHAO, Y. LI and K. CHENGSHAN, *Appl. Surf. Sci.* **193** (2002) 87.
11. S.-I. KITAZAWA, A. NAITO, C. LIN and H. NARAMOTO, *J. Cryst. Growth* **267** (2004) 336.
12. Y. Q. ZHOU, Z. J. CHEN, H. JIN, P. ZHENG and W. H. WANG, *ibid.* **204** (1999) 289.
13. X. JIANG, T. HERRICKS and Y. XIA, *Nano Lett.* **2** (2002) 1333.
14. R. MORONI, F. BISIO, M. CANEPA and L. MATTERA, *Surf. Sci.* **454–456** (2000) 875.
15. D. QIAN, G. L. LIU, D. LOISON, G. S. DONG and X. F. JIN, *J. Cryst. Growth* **218** (2000) 197.
16. C. KAITO, H. NAKAMURA, S. KIMURA, Y. KIMURA, T. NAKADA and Y. SAITO, *Thin Solid Films* **359** (2000) 283.
17. S. TSUKIMOTO, F. PHILLIPP and T. WAGNER, *J. Eur. Ceram. Soc.* **23** (2003) 2947.
18. M. R. FITZSIMMONS, J. A. EASTMAN, R. A. ROBINSON, A. C. LAWSON, J. D. THOMPSON, R. MOVSHOVICH and J. SATTI, *Phys. Rev. B* **48** (1993) 8245.
19. W. S. ZHANG, E. BRUCK, Z. D. ZHANG, O. TEGUS, W. F. LI, P. Z. SI, D. Y. GENG and K. H. J. BUSCHOW, *Physica B* **358** (2005) 332.
20. Q. DONG, J. HU, Z. GUO, J. LIAN, J. CHEN and B. CHEN, *Appl. Surf. Sci.* **202** (2002) 114.
21. Q. FU and T. WAGNER, *Thin Solid Films* **420/421** (2002) 455.
22. E.-P. KIM, T.-H. KIM, S.-T. KIM, Y. KUK and S.-J. KIM, *Thin Solid Films* **441** (2003) 317.

Received 4 May  
and accepted 29 August 2005