行政院國家科學委員會專題研究計畫成果報告

分子化合物合成無機材料之新方法 (3) NEW MOLECULAR ROUTES TO INORGANIC MATERIALS (3)

計畫編號: NSC 90-2113-M-009-022

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中文摘要

本報告摘要第三年國科會計畫之研究 發現。主要為合成 TiC, Mo, W, Cu 奈米顆 粒, C 薄膜及柱, 與化學氣相沉積薄膜之表 面化學反應機制研究。

關鍵詞: 奈米顆粒、薄膜、化學氣相沉積、 表面化學反應

Abstract

This report summarizes the research activities discoveries of the third year of the project supported by the NSC. Major discoveries include new methods to prepare TiC, Mo, W and Cu nanoparticles, C thin film and nanorods materials, new precursors and surface reaction studies of CVD.

Keywords: nanoparticles, thin films, chemical vapor deposition, surface reaction

Introduction

Chemical reactions to nanosized inorganic materials are under intensive investigations for their special chemical and physical properties. In this study, we will demonstrate several new synthetic strategies to prepare these materials. We have also performed fundamental surface reaction studies of several chemical vapor deposition (CVD) precursors using Synchrotron

Radiation Based X-ray Photoelectron Spectroscopy. Our discoveries will be discussed below briefly.

Summary

Preparation of New Precursors and Routes to Inorganic Thin Films [1].

Complexes Me₃CE=Ta(CH₂CMe₃)₃, (E = CH, N), have been prepared and employed as CVD precursors to grow thin films of TaC and TCN. Some representative AFM images (Figures 1 and 2) are shown below.

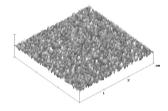


Figure 1. AFM surface morphology of the film deposited at 623 K from $Me_3CCH=Ta(CH_2CMe_3)_3$ in H_2 .

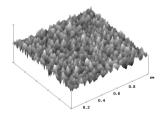


Figure 2. AFM surface morphology of the film deposited at 773 K from $Me_3CN=Ta(CH_2CMe_3)_3$ in H_2 .

Surface Reaction Studies CVD Precursors on Surface [2-3]. We used SR-XPS and

TPR to study the surface reactions of several precursors on different surfaces and found that different surfaces affect the film composition significantly (Figures 3 and 4).

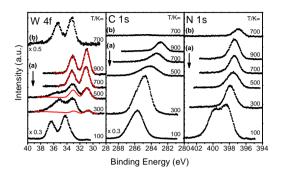


Figure 3. SR-XPS spectra for (a) 3 L BTBTT dosed and annealed to high temperatures on Si(100), and (b) 1 L BTBTT dosed and annealed to 700 K on Cu(111). The X-ray energy is 600 eV. For clarity, only the W(0) component from the peak fit is shown in W 4f signal.

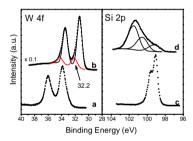


Figure 4. W 4f and Si 2p SR-XPS spectra obtained after a dosing of 5 L of BTBTT on Si(100) at 100 K (a & c) and after a simulated CVD run (see text for details) at 900 K (b & d). The X-ray energy is 200 eV.

Preparation of Nanosized Transition Metal Materials by New Routes [4-5].

Several new synthetic methods have been explored. We have discovered that transition metal nanoparticles can be synthesized at low temperatures from metal complexes and organopolysilane oligomers (Figure 5).

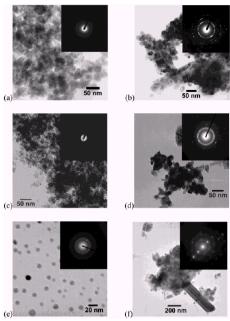


Figure 5. TEM and ED images of (a) Mo nanoparticles prepared at 473 K and (b) annealed at 1273 K. (c) W nanoparticles prepared at 573 K and (d) annealed at 873 K. (e) Cu nanoparticles prepared at 343 K and (f) annealed at 523 K.

Also, we found that titanium metal can be nanosized into titanium carbide by reacting with 1-chlorobutane (Figure 6).

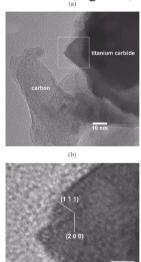




Figure 6. TEM studies of a TiC crystal obtained at 1273 K, (a) TEM image, (b) HRTEM image of the selected area shown in (a), and (c) ED pattern.

New Synthetic Strategy for Carbon Materials [6 - 8].

Carbon materials are important for many technology uses. We explored using small molecules as the building blocks for interesting carbon materials, including nanographites, onions, nanorods, and thin films. We explored a new strategy called "Polygon Building Block Route to sp2 Carbon Based Materials". The results are shown in Figures 7 and 8.

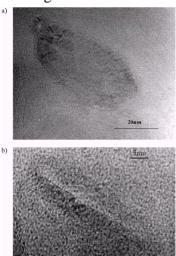


Figure 7. (a) HRTEM of spherical and elliptical carbon onions. (b) HRTEM of a rod-shaped carbon onion.

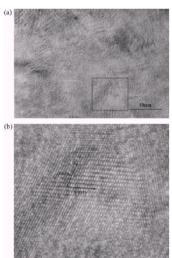


Figure 8. (a) HRTEM image of the graphite powder. (b) Enlarged HRTEM image of the rectangular region shown in (a).

Also, coupling C6Cl6 using Li as the reductant can form carbon rods (Figure 9).

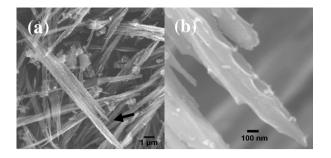
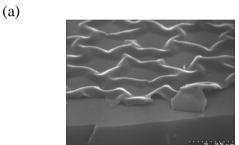


Figure 9. SEM images of carbon rods: (a) low and (b) high magnification.

We also discovered that SiCl₃CCl₃ can be employed as a novel precursor to deposit amorphous carbon films (Figure 10).



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Figure 10. SEM images of carbon films prepared at (a) $773~\mathrm{K}$ and (b) $1173~\mathrm{K}$.

References

(b)

1. Y.-H. Chang, J.-B. Wu, P.-J. Chang, and H.-T. Chiu, "Chemical Vapor Deposition of Thin Films from Me₃CE=Ta(CH₂CMe₃)₃, (E = CH, N)", *J. Mater. Chem.*, in press.

2. J.-B. Wu, Y.-W. Yang, Y.-F. Lin, H.-T. Chiu, "Surface Reaction of Bis(tertbutylimido)bis(diethylamido)tungsten Precursor on Si(100) - (2 X 1)", submitted.

3. J.-B. Wu, Y.-F. Lin, H.-T. Chiu, Y.-W. Yang, "From Surface Reaction to Chemical Vapor Deposition: Thermal Decomposition of Bis(tertbutylamido)bis(tertbutylimido)-

- tungsten on Si(100)", submitted.
- 4. Y.-H. Chang, H.-W. Wang, C.-W. Chiu,
- D.-S. Cheng, M.-Y. Yen, and H.-T. Chiu,
- "Low-Temperature Synthesis of Transition
- Metal Nanoparticles from Metal Complexes
- and Organopolysilane Oligomers", *Chem. Mater.*, 2002, **14**, 4334.
- 5. Y.-H. Chang and H.-T. Chiu, "Nanosizing
- Titanium into Titanium Carbide by
- 1-Chlorobutane", *J. Mater. Res.*, 2002, **17**, 2779.
- 6. C.-Y. Lee, H.-T. Chiu, C.-W. Peng, M.-Y.
- Yen, Y.-H. Chang and C.-S. Liu, "Polygon
- Building Block Route to sp2 Carbon Based
- Materials", Adv. Mater., 2001, 13, 1105.
- 7. Y.-H. Chang, H.-T. Chiu, L.-S. Wang,
- C.-Y. Wan, C.-W. Peng and C.-Y. Lee,
- "Synthesis of Carbon Rods by Coupling
- C₆Cl₆ Using Li as the Reductant", submitted.
- 8. Y.-H. Chang, L.-S. Wang, H.-T. Chiu and
- C.-Y. Lee, "SiCl₃CCl₃ as a Novel Precursor
- for Chemical Vapor Deposition of
- Amorphous Carbon Films", *Carbon*, in revision.

附件:封面格式

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