Stripping Off the Halogens:  
From Silylenes to Metal Silicides to Nanocarbons

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Abstract

Halides were used as the precursors to prepare various kinds of materials by stripped off the halogens. Metals, metal silicides and carbon related materials could be prepared by using metal halides, silicon halides and carbon halides as the precursors. Some active metals and active meta stable species were used as stripping reagents.

Key Words: Halides, Reduction, Silicides, Carbon Oinions.

1. Introduction

Stripping off the halogens from halides has been a trick commonly and repeatedly used by chemists of different disciplines to synthesize new molecules of a great variety of forms. The Wurtz type reaction, frequently used by organic chemists, is a typical example of halogens stripped reaction. This paper reports our journey to discover the chemistry of silylenes, an intermediate species generated by stripping off the halogens from the silanes, which is in turn used to strip off the halogens of metal halides to form metal silicides. And some reactive metals was used, we show how meta stable precursors can be prepared in situ by stripping off the halogens from metal halides when more powerful “halogen-scavengers” are involved.

2. Experimental

2.1 General Synthesis Steps of Carbon Related Materials

The selected precursor, either C₅Cl₆ or C₆Cl₆, was allowed to react with a stoichiometric amount of Na in a tube (allow extra volume for potential expansion of the vaporized precursors) sealed under vacuum at ca. 100 – 150 °C. A dark gray powder was formed immediately from the highly exothermic reaction. After the reaction ceased, the byproduct NaCl was removed by washing with water. A black powder composed of carbon, as suggested by elemental analysis and EDS (energy dispersive spectroscopy), was isolated in nearly quantitative yield. Solid-state ¹³C NMR spectra showed resonance signals assignable to order and disorder carbons with a relative intensity ratio of 7:3 for the reaction of Na and C₅Cl₆; 1:2 for the reaction of Na and C₆Cl₆ [12].

2.2 General Procedure of Chemical Vapor Deposition Reaction

Deposition reactions were performed in a low pressure hot wall reactor. The reactor consists of a pumping system, reaction chamber and precursor inlet system. The reactor consisted of a 30 mm inside diameter removable quartz tube and a tube furnace. Substrates used were Si(100), graphite and SiO₂. Thin films grown on graphite substrates were used for composition measurement.

The precursors, metal halides, were used as received. The silicon substrates were cleaned by the standard RCA procedures to remove grease and the oxide was etched off just before loading. The quartz substrates were washed with household detergent, distilled water, and finally dried at 120 °C for 10 min. The reaction and substrate temperature was measured with a K-type TC gauge. The inlet quantity of precursors was measured by mass flow controller.
The general procedure for a deposition run was, first, to evacuate the system to the pressure of $10^{-2}$ Pa. Then the system evacuated to $10^{-3}$ Pa, the precursors were introduced into the reactor at room temperature. The deposition period is 2 h.

The volatile products that were collected by a liquid nitrogen trap were analyzed by infrared and mass spectra. The thin films were characterized by scanning electron microscopy for the morphologies and were analyzed by energy dispersive spectroscopy for the composition. The microstructure of the thin films were characterized by X-ray diffraction pattern. X-ray photoelectron spectroscopy was used to characterize the chemical environment of the thin films. Auger electron spectroscopy was used to obtain depth composition profiles of the thin films.

2.3 Characterization of the Reaction Products

SEM micrographs were obtained in a JEOL 840A SEM microscope with EDS analytical capability. X-ray diffraction (XRD) patterns of the thin films were taken with Cu Kα radiation using a Siemens D5000 diffractometer. Infrared spectra were obtained on a Perkin-Elmer PC2000 IR spectrometer. The GCMS data were obtained by a Shimadzu QP1000 spectrometer. X-ray photoelectron spectra (XPS or ESCA) were measured on a Physical Electronics PHI 1600 ESCA spectrometer. Auger electron spectra (AES) were measured on a Physical Electronics 670 PHI Xi Auger spectrometer.

3. Results and Discussion

The first work is to deposit tungsten related materials by using WF₆ and SiF₂ as the precursors. In a low-pressure chemical vapor system, we deposited tungsten based thin films on a substrate, using a horizontal hot-wall reactor. WF₆ and SiF₂ were used as precursors to deposit materials containing tungsten, to a temperature between 100 °C and 800 °C. Results demonstrate that a deposition temperature below 400 °C deposited polycrystalline tungsten and silicon oxide. Tungsten films deposited at higher temperature (300–400 °C) were normally present in the α structure. For those tungsten films deposited at lower temperature (< 300 °C), XRD patterns indicated mixed α and β phases. As the reaction temperature rose above 500 °C, polycrystalline tungsten silicide and polycrystalline silicon were deposited on the substrate's surface. This study investigates the effect of different processing conditions for forming W and WSi₂, and the role of SiF₂ in forming W and WSi₂ [2].

The pathway of the formation of W and WSi₂ films can be shown as follows.

$$\text{SiF}_2 + \text{WF}_6 \xrightarrow{100 \sim 400 \, ^\circ \text{C}} \text{W} + \text{SiF}_4$$

$$\xrightarrow{500 \sim 800 \, ^\circ \text{C}} \text{WSi}_2 + \text{poly-Si}$$

In this reaction, difluorosilylene acts as a halogen “scavenger” (for the tungsten metal formation at low temperature condition) and as a silicon source (for the silicide formation at high temperature condition).

On the other hand, if TaX₅ (X = Cl, F) was used instead of WF₆ in the deposition reaction, polycrystalline TaSi₂ was obtained at 200 °C. This is the lowest deposition temperature of metal silicides in literature. The pathway of the formation of TaSiₓ films can be shown as follows.

$$\text{TaX}_2 + \text{SiF}_2 \rightarrow \text{TaSi}_x$$

$$X = F, Cl$$

In this reaction, difluorosilylene acts both as a silicon source (the first step of the scheme) and as a halogen “scavenger” (the second step of the scheme).

Transition metals halides were not the only halide group reacted with silylene, main group halides react with silylene too. GeₓSi₁₋ₓ thin films (x = 0.03–0.75) were grown on Si (111), quartz and graphite by LPCVD using SiF₂ and GeCl₄ as the precursors at 450–700 °C. Thin films prepared at 550–700 °C contained polycrystalline GeₓSi₁₋ₓ. The composition of the thin film can be controlled...
by adjusting reaction temperature and the relative inlet quantity of GeCl₄. A linear correlation between the lattice parameters of the GeₓSi₁₋ₓ thin films prepared and the Ge contents x is established. A plausible reaction mechanism can be proposed to account for all the products observed in the reaction [3]:

\[
\begin{align*}
2 \text{SiF}_2 & \rightarrow \text{SiF}_4 + \text{Si} \\
\text{SiF}_2 + \text{GeCl}_4 & \rightarrow \text{Ge} + \text{SiF}_4\text{Cl}_n \\
\text{Ge} + \text{Si} & \rightarrow \text{Ge}_x\text{Si}_{1-x}
\end{align*}
\]

The dual role of SiF₂ both as a silicon source for the thin film produced as well as a scavenger of F and Cl, is shown in this reaction too. In lower temperatures the disproportionation of SiF₂ is the dominating reaction; in higher temperatures the chlorine abstraction (to form Ge) becomes the major reaction.

Difluorosilylene is not the only species occur disproportionation reaction to form important materials. Another example is to deposit titanium thin films using Ti metal and titanium tetrachloride as the precursors. In this work, we deposited titanium based thin films by a low pressure chemical vapor deposition system on a substrate using a horizontal hot-wall three zone reactor. TiCl₄ and a titanium metal plate were used as the precursors to in situ prepare TiCl₄ (n = 1, 2, 3) at the first zone with a reaction temperature of 900 °C. The deposition reaction occurred at a temperature exceeding 550 °C at the third zone. Experimental results indicated that the composition of thin films is a titanium metal on stainless steel, polycrystalline C₅₄-TiSi₂ on silicon wafer. According to our results, titanium silicide grown on quartz is easily dissolved in dilute acid, allowing for selective deposition of titanium disilicide on silicon wafer at an extremely mild condition (550 °C). In this process, no chlorine gas is detected and no hydrogen gas is used; the only volatile component is titanium tetrachloride. This component can be collected and reused. Deposition of titanium from TiCl₄ in a thermal process at 1200 °C is impossible under conditions compatible with fabricating integrated circuits. Above results confirm that the proposed method that deposit titanium at 550 °C is highly promising for further device fabrication.

And finally, we show how nanocarbon materials can be prepared in bulk by stripping off the halogens from halocarbons when more powerful “halogen-scavengers” are involved. The proposed reaction mechanism for preparing amorphous carbon by reacting of carbon tetrachloride with sodium can be shown as follows.

\[
\begin{align*}
\text{Na} + \text{CCl}_4 & \rightarrow \text{CCl}_3 + \text{NaCl} \\
\text{Na} & \rightarrow \text{C} + \text{NaCl}
\end{align*}
\]

In an analogous reaction employing C₅Cl₆ and C₆Cl₆, respectively, as the building blocks, we have shown that carbon onions and nano-sized graphite can be synthesized shown in Figure 1.

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Figure 1. (a) The HRTEM image of nano-graphite obtained by reaction of Na and C₆Cl₆. (b) The HRTEM image of carbon onions obtained by reaction of Na and C₅Cl₆.
The proposed reaction mechanism for the reaction of \( \text{C}_6\text{Cl}_6 \) with sodium can be shown as follows [4].

\[
\begin{array}{c}
\text{C}_6\text{Cl}_6 + \text{Na} \rightarrow \text{C}_6\text{Cl}_6^- + \text{NaCl} \\
\end{array}
\]

And the proposed reaction mechanism for the reaction of \( \text{C}_5\text{Cl}_6 \) with sodium can be shown as follows [4].

\[
\begin{array}{c}
\text{C}_5\text{Cl}_6 + \text{Na} \rightarrow \text{C}_5\text{Cl}_6^- + \text{NaCl} \\
\end{array}
\]

In conclusion, we have shown that carbon onions and nano-sized graphite can be synthesized employing carefully selected precursors, \( \text{C}_6\text{Cl}_6 \) and \( \text{C}_5\text{Cl}_6 \), respectively, as the building blocks. It is promising that the “building block” strategy can be applied to prepare other carbon-based materials by selecting suitable precursors and reaction conditions.

4. Conclusion

Simple and useful way to prepare materials is developed by using halides as the precursors to be stripped off the halogens. By selecting suitable precursors and reaction conditions, the materials can be prepared under very mild condition with cheap equipment.

References


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