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# A convenient thermal decomposition-co-reduction synthesis of nanocrystalline tungsten disilicide

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**Abstract. Nanocrystalline $WSi_2$ was synthesized by a thermal decomposition-co-reduction route via the reaction of anhydrous tungsten hexachloride and sodium fluorosilicate with metallic potassium in an autoclave at 650°C. X-ray powder diffraction pattern indicated that it was tetragonal $WSi_2$. Transmission electron microscope image showed that it consisted of particles with an average diameter of about 50 nm. TGA and DTA indicated that it had good thermal stability below 600°C in air.**

**Keywords. Nanostructures; tungsten disilicide; chemical synthesis; X-ray diffraction; thermal analysis.**

## 1. Introduction

As a class of materials, transition metal silicides have recently been the focus of considerable attention for potential application as structural high temperature materials to be used at $T > 1000$°C (Petrovic 1997). Meanwhile, the development of sub-micron integrated circuit devices has gained considerable attention and success in semiconductor technology in recent years. In particular, refractory-metal silicides also have attracted considerable interest with regard to the possibility of using them as a gate and interconnect metallization material in fabricating semiconductor devices (Crowder and Zirinsky 1979a; Mohammadi and Saraswat 1980; Gcipel Jr *et al* 1980). Due to the outstanding material properties of high-temperature stability and low electric resistivity, tungsten silicide is generally considered to be one of the most important refractory-metal silicides. Most of the $WSi_2$ materials are in the form of thin films. But it is meaningful to synthesize nanocrystalline $WSi_2$ as the nano-sized powders can reduce the sintering temperature (Yeh and Sacks 1988) for bulk materials.

Traditionally, tungsten silicide can be prepared by various methods such as reacting tungsten metal with silicon in high temperatures (Locker and Capio 1973), co-evaporating tungsten and silicon (Crowder and Zirinsky 1979b), co-sputtering tungsten and silicon (Chow *et al* 1983), sputtering from a target made of tungsten silicide (Mohammadi and Saraswat 1980), depositing chemical vapours (Brors *et al* 1983) and synthesizing by ion beams (While *et al* 1987). A carbothermal reduction process (Hojo and Ishizaka 1997) can also prepare $WSi_2$ powder.

In this paper, nanocrystalline tungsten disilicide has been synthesized by a convenient thermal decomposition-co-reduction route via the reaction of metallic potassium with sodium fluorosilicate and tungsten hexachloride in an autoclave at 650°C. This reaction can be described as follows

$$WCl_6 + 2Na_2SiF_6 + 14K \rightarrow WSi_2 + 4NaF + 8KF + 6KCl.$$

## 2. Experimental

Typically, 0·01 mol anhydrous $WCl_6$ and 0·02 mol $Na_2SiF_6$ were placed in a quartz tube. Then about 0·15 mol metallic potassium was added in the quartz tube. The quartz tube was put into stainless steel autoclave and sealed under argon atmosphere. The autoclave was heated at 650°C for 10 h, followed by cooling to room temperature in the furnace. The obtained products from the quartz tube were washed several times with 0·1 M hydrochloric acid, 0·1 M alkali solution, distilled water and absolute ethanol to remove impurities. The final product was vacuum-dried at 60°C for 12 h.

The powder product was analysed by powder X-ray diffraction (XRD) on an X-ray diffractometer (Rigaku rA) using CuK$\alpha$ radiation (wavelength, $l$ = 1·54178 Å), and transmission electron microscopy (TEM) on a Hitachi 800 transmission electron microscope. The thermal analysis was performed on a thermal analyser (Model: TA-50) below 1000°C in air at a rate of 10°C·min$^{-1}$ to study the oxidation behaviour of the sample.

## 3. Results and discussion

Figure 1 shows the XRD pattern of the as-prepared sample. All the diffraction peaks at different $d$-spaces can be in-

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dexed as the tetragonal tungsten disilicide phase (002, 101, 110, 103, 004, 200, 114, 211, 006, 213, 204). After refinement, the lattice constants are $a = 3{\cdot}225$ Å and $c = 7{\cdot}872$ Å, which are very close to the reported values for $WSi_2$ ($a = 3{\cdot}212$ Å and $c = 7{\cdot}880$ Å, JCPDS card, No. 74-1149). No evidence of impurities such as W, Si, $SiO_2$ and tungsten oxides can be found in the XRD pattern.

Figure 2 shows the transmission electron microscopy (TEM) image of the sample. It can be seen that the sample consists mainly of nanoparticles. From the image, the sample exhibits a slightly agglomerated morphology due to the fine size of the particles. The nanocrystalline $WSi_2$ particles produced from the present route typically have the diameters of 40–60 nm and an average diameter of about 50 nm. We also investigated the thermal stability of these nanosized powders in flowing air. The oxidation process of nanocrystalline $WSi_2$ was studied at temperatures below 1000°C under flowing air by TGA and DTA, as shown in figure 3.

From the TGA curve, we can find that the weight of the product has not changed significantly below 600°C. A slight weight loss indicates that the sample might adsorb a little water on the surface. But the quantity of the adsorbed water is very small, and we cannot find any endothermic peak on the DTA curve within the corresponding temperature. From 600–900°C, the weight of the powders increases gradually by about 41·0%, which is close to the calculated value after thoroughly oxidizing. On the DTA curve, there is only one big exothermic peak centred at the temperature of 700°C. Combining the results of the two curves, we can reach the following conclusion. The sample has basically not been oxidized from room temperature to 600°C. From 600°C on, the sample suffers gradual oxidation on its surfaces. The oxidation process becomes intensified as the temperature rises to 700°C, forming an exothermic peak on the DTA curve. From 900°C on, there is a platform on the TGA curve, indicating no weight change. And from the XRD pattern of the sample tested by TGA/DTA, we cannot find evidence of $WSi_2$. The sample can be oxidized thoroughly at 900°C. In the oxidation of silicides, sufficient concentration of Si for the formation of a protective $SiO_2$ scale is required. And this scale must be in plasticity (Kurokawa *et al* 2002). Probably, $SiO_2$ formed in our test was fragile and porous, resulting in further oxidation. From above results, the sample has good thermal stability below 600°C.

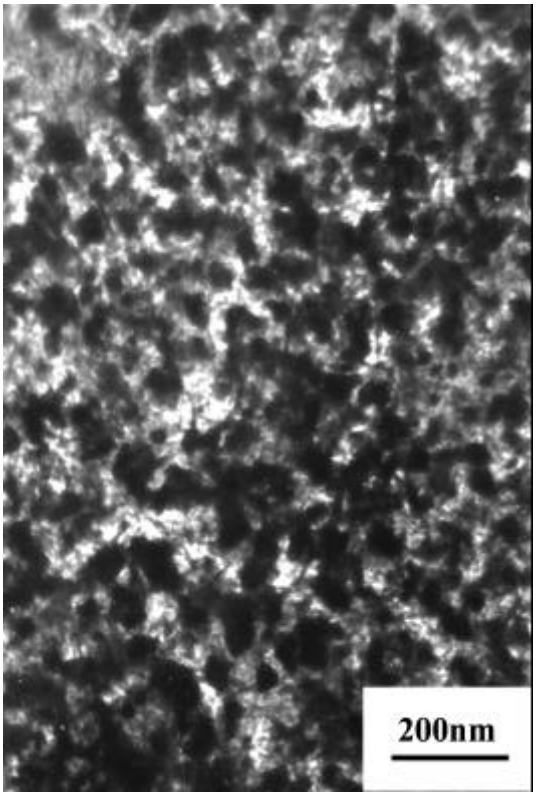


**Figure 2.** TEM image of the as-prepared $WSi_2$ sample.

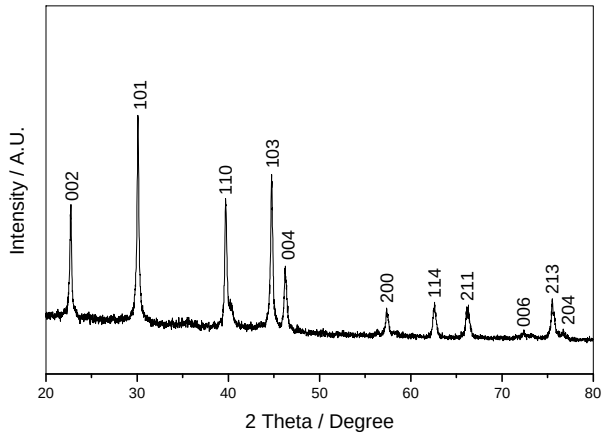


**Figure 1.** XRD pattern of the as-prepared sample.

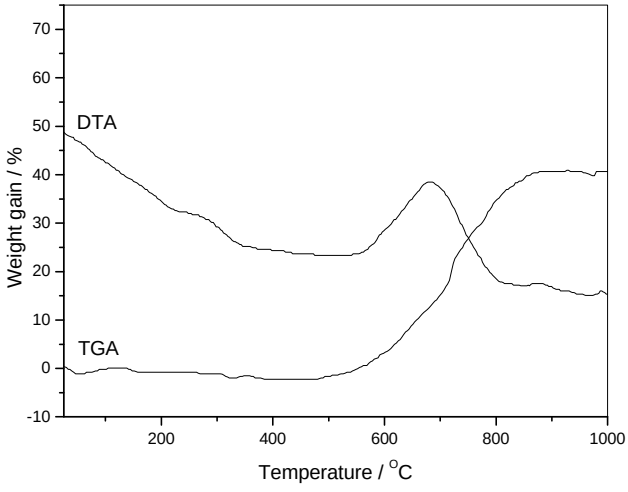


**Figure 3.** TGA/DTA curves of $WSi_2$ heated in flowing air.

In the whole reaction process along with the increase of temperature, sodium fluorosilicate can decompose into sodium fluoride and gaseous silicon tetrafluoride above 400°C. So it is believed that the synthetic reaction of tungsten disilicide is based on the reduction of anhydrous tungsten hexachloride and silicon tetrafluoride by metallic potassium. The formation process of tungsten disilicide can be described as follows:

$$Na_2SiF_6 \rightarrow 2\ NaF + SiF_4,$$
$$SiF_4 + 4\ K \rightarrow Si^* + 4\ KF,$$
$$WCl_6 + 6\ K \rightarrow W^* + 6\ KCl,$$
$$W^* + 2\ Si^* \rightarrow WSi_2.$$

In this route, NaF, KF and KCl can be formed as by-products. The melting point of the salt system is about 605–606°C. Since the reaction temperature is above this melting point, the reaction, in which nascent tungsten (W*) combines with nascent silicon (Si*) to form tungsten disilicide, can be carried out in this molten salt system. The molten salt helps to form the nanocrystalline tungsten disilicide.

## 4. Conclusions

In summary, nanocrystalline tungsten disilicide has been successfully prepared via a convenient decomposition-co-reduction route by the reaction of metallic potassium with anhydrous tungsten hexachloride and sodium fluorosilicate in an autoclave at 650°C. The product has the tetragonal tungsten disilicide structure, and the particles have diameters of 40–60 nm and an average diameter of about 50 nm. The sample is very stable in air below 600°C.

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