

# PRODUCTION OF NANOPOWDERS BY HYSYCVD

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## Abstract

A Novel route for in situ synthesis of nanopowders via the hybrid precursor system chemical vapor deposition (HYSYCVD) has been developed. The route is based on the thermal dissociation of a solid precursor with the subsequent reactions in gas phase, reason for which it has been referred to as HYSYCVD. In this contribution, the authors present the essentials of this route and its advantages when compared with other synthesis routes. As an illustration, optimal conditions for selectively promoting the synthesis of nano-size powders of silicon nitride are also outlined.

## Introduction

The recent boom undergone by nano-science and nanotechnology has stimulated the development of a large number of processing routes for a variety of materials, ranging from metals and intermetallics to ceramics and composites. However, the routes are grouped into six widely known methods to produce nanomaterials other than by direct atom manipulation, namely, sol-gel synthesis, ball milling, electrodeposition, plasma arcing and chemical vapor deposition (CVD). The use of natural nanoparticles is also considered to be included within the 6 methods [1]. Other forms of classification include chemical synthesis routes, sputtering, thermal evaporation and laser methods [2]. Liquid phase chemistry methods are considered apart because they can be used to prepare the precursor, which is subsequently converted to nanoscale particles by non-liquid phase chemical reactions.

The chemical vapor deposition (CVD) route has for a long time been considered highly attractive for several reasons, but it stands out due to the high purity of the final products. In CVD a material is heated to form a gas and then allowed to deposit as a solid on a surface, usually under vacuum. There may be direct deposition or deposition by chemical reaction to form a new product which differs from the material volatilized [3]. Other factors that should be taken into consideration are connected to the particular variant of the CVD process, especially because during the last decade, many modifications have proliferated. When assessing the viability of a new CVD route it is always important to consider the various processing parameters mentioned above, as well as availability, environmental and safety aspects of gas precursors. This is in addition to cost. As for environmental and safety issues, the use of stable solid precursors functioning as stores for the generation of other gas species – to take part in CVD process –

when required in time and space, was the motivation for the present contribution.

The proposed route is based on the in situ thermal dissociation of a solid precursor and the formation of nanometric size powders through gas phase reactions with an appropriate gas precursor. This route was developed recently at CINVESTAV-SALTILLO (Cinvestav is the Spanish acronym of Center for Research and Advanced Studies, Saltillo is the location city, Northeast Mexico). It was originally termed the hybrid precursor system chemical vapor deposition (HYSYCVD) by the inventors.

This method is based on the ability of some solids like sodium hexafluorosilicate ( $\text{Na}_2\text{SiF}_6$ ) to produce highly reactive gas species ( $\text{SiF}_3$ ,  $\text{SiF}_2$ ,  $\text{SiF}$  and  $\text{Si}$ ) which, by the reaction with other proper precursors (for instance, nitrogen precursors), allow the formation of condensed phases as stable solids [4]. Nanoscale advanced ceramics, such as  $\text{Si}_3\text{N}_4$ , as well as  $\text{Si}_2\text{N}_2\text{O}$  can be produced under suitable processing conditions.

## Experimental procedures

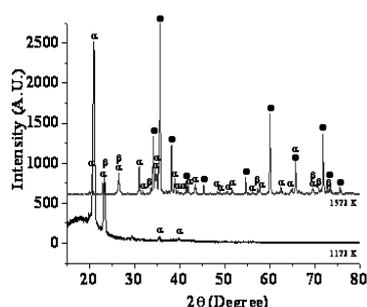
In this particular paper, formation of silicon nitride is used as an illustration of the application of the method. Synthesis trials are carried out in the conventional CVD reactor described elsewhere [5]. The processing parameters time, temperature, pressure and amount of  $\text{Na}_2\text{SiF}_6$  were studied at two levels (60 and 120 minutes, 1173 and 1573 K, 17 and 19 mbars, and, 0 and 25 g, correspondingly). The solid precursor compacts ( $\text{Na}_2\text{SiF}_6$ ) are located near the reactor entrance, where the temperature can be varied in the dissociation temperature range of the solid precursor (for  $\text{Na}_2\text{SiF}_6$ , between 386-578 and 465-873 K). The substrates, on the other hand, are placed within the reactor in specific positions, according to the predetermined deposition temperature, and treated either in high purity nitrogen (HPN) or a high purity mix of  $\text{N}_2$ - $\text{NH}_3$  (50:50). The substrates consist of  $\text{SiC}_p/\text{Si}$  cylindrical performs (37 mm in diameter x 25.4 mm long) with 50 % porosity prepared by the uniaxial compaction of the corresponding powders, both with an average particle size of 25  $\mu\text{m}$ .  $\text{SiC}_p$  and  $\text{Si}$  powders within the preform are used in the proportion 85:15 wt. %, respectively. For  $\text{Si}_3\text{N}_4$  formation, the substrates temperatures are controlled between 1173 and 1573 K. Processing temperature and substrate temperature are two different parameters considered in the experiment. As both the solid precursor dissociation and the new phase formation occur in the same reactor, the synthesis route is referred to as an *in situ* process [4]. Nanoscale powders of the new phase can be deposited into porous substrates, on

flat monolithic substrates or collected at the reactor's exit as powders.

As described in previous publication [5], the reactor is divided into three different zones, namely, precursor dissociation (zone I), new phase formation (zone II) and new phase deposition (zone III). Once the solid precursor and the substrates are placed in their corresponding positions, the reactor is closed and the system is heated at a rate of 15 °C/min either in ultra high purity (UHP) nitrogen in the N<sub>2</sub>-NH<sub>3</sub> mix, up to the test temperature, maintained isothermally for the corresponding test time (according to the experimental design) and cooled down to room temperature at 15 °C/min. After cooling down to room temperature, the substrates are removed from the reactor for microstructure characterization using Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), scanning electron microscopy (SEM) provided with energy dispersive X-ray spectroscopy (EDX), and transmission electron microscopy (TEM).

## Results and discussion

Although Si<sub>3</sub>N<sub>4</sub> was detected in specimens treated in both atmospheres, results show that the presence of ammonia enhances formation of this phase. In Fig. 1 X-ray diffraction patterns of samples obtained in the center and the cylindrical surface of a specimen – processed at 1300 °C for 120 min in nitrogen at a pressure of 17 mbar –, are shown respectively. Both, α-Si<sub>3</sub>N<sub>4</sub> and β-Si<sub>3</sub>N<sub>4</sub> polymorphs are typically formed with the morphology of particles, fibers/whiskers and coatings on the SiC particles.



**Fig. 1** X-ray diffraction patterns showing the presence of α- and β- silicon nitride.

While in the atmosphere containing ammonia, silicon nitride can be formed from a 10 min test time, in nitrogen it is detected only after 90 min. In the case of Si<sub>3</sub>N<sub>4</sub> whiskers/fibers, it is observed that their size is larger when using ammonia and typically, fibers with an

average diameter of 2.3 μm are produced. For both atmospheres, the longer the test time, the larger the amount of Si<sub>3</sub>N<sub>4</sub> deposited and the diameter of the whiskers formed. The benefit obtained with ammonia can be explained in light of its thermal and chemical stability. The ionization potentials for N<sub>2</sub> and NH<sub>3</sub> are 15.576 eV and 10.2 eV, respectively [4].



**Fig. 1** Si<sub>3</sub>N<sub>4</sub> nano-ribbons obtained by HYSYCV

## Summary and conclusions

Results from this investigation show that the hybrid precursor system chemical vapor deposition (HYSYCV) allows the formation of fibers and powders with submicron or nanometric size and, that specific morphology and size can be promoted by appropriate control of processing parameters. Interestingly, nanometric size products can be obtained simply in nitrogen, because the N<sub>2</sub>-NH<sub>3</sub> mix tends to increase the product growth. Current work using other solid precursors suggests the potential for the preparation of TiN and BN – amongst other phases – using the same processing route.

## References

- [1] M. Wilson, K. Kannangara, M. Simmons, B. Raguse, Nanotechnology Basic Science and Emerging Technologies, Chapman & Hall/CRC, New York, NY, 2002.
- [2] A. S. Edelstein and R. C. Cammarata, Editors, Nanomaterials: Synthesis, Properties and Applications, Taylor and Francis, New York, NY, 1996.
- [3] J.-H. Park, Editor, Chemical Vapor Deposition, ASM International, Materials Park, OH, USA, 2001.
- [4] A. L. Leal-Cruz, M. I. Pech-Canul, In situ synthesis of Si<sub>3</sub>N<sub>4</sub> from Na<sub>2</sub>SiF<sub>6</sub> as a silicon solid precursor, Mat. Chem. and Phys., 2006, **98**, 27-33.
- [5] A. L. Leal-Cruz, M. I. Pech-Canul and J. L. de la Peña, A low-temperature and seedless method for producing hydrogen-free Si<sub>3</sub>N<sub>4</sub>. Rev. Mexicana de Física, 2008, **54** (3), 200-207.