Novel synthesis of nitride powders by microwave-assisted combustion

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A novel and simple microwave-assisted combustion procedure for the synthesis of a number of technologically important metal nitrides was demonstrated. The method involves the combustion reaction of a porous metal powder compact with N\textsubscript{2} gas in the microwave field and provides phase-pure metal nitride products (consisting of fine particles, fibers, and whiskers) within minutes. The ignition and combustion temperatures of the reaction were found to vary as a function of compaction pressure. The microwave-prepared nitrides were characterized using x-ray diffraction, scanning electron microscopy energy dispersive spectroscopy, thermogravimetric analysis, and infrared spectroscopy. The present microwave-assisted hybrid-heating procedure allows the preparation of nitrides with good crystallinity, structural uniformity, and phase purity, and appears to have general applicability for the preparation of metal nitrides (using the respective metals or even their oxides).

I. INTRODUCTION

Metal nitrides possess very high thermal, mechanical, and chemical stability.\textsuperscript{1} Several nitrides are also characterized by low densities and are therefore of great technological interest for light-weight applications. Titanium nitride (TiN) is a well-known diffusion barrier for aluminum interconnect metallization in very large-scale integration (VLSI) device technology.\textsuperscript{2} It is also used as a gold-colored hard coating on many tool parts.\textsuperscript{3} Aluminum nitride (AlN) has attracted much attention in recent years for its excellent dielectric properties, high thermal conductivity, high-temperature machinability, and good electrical resistivity.\textsuperscript{4,5} AlN is also an electronic substrate material due to its good thermal compatibility and non-reactivity with silicon.\textsuperscript{6} Vanadium nitride (VN) is an important industrial catalyst known for its selectivity and stability.\textsuperscript{7} Gallium nitride (GaN) is one of the most promising wide-band-gap (3.38 eV) materials for short-wavelength optoelectronic devices and has potential for applications in high-temperature electronics and in realizing blue-ultraviolet lasers. Commercial nitride powders are synthesized via either carbothermal\textsuperscript{8} or direct nitridation\textsuperscript{9} of metals. The conventional procedures for the synthesis of these important nitrides, however, are often plagued by extremely long reaction times (several hours to even days) caused by slow diffusion rates in solids and usually involve many cumbersome steps. They often require the use of atomized metal powders (involving risk of explosions),\textsuperscript{10} laser heating at high pressures,\textsuperscript{11} very precise temperature-programmed reaction controls,\textsuperscript{12} heating of the respective oxides for several hours in a continuous flow of ammonia,\textsuperscript{13} and so on. Besides these, other methods on laboratory-scale synthesis have been reported, such as decomposition of expensive organometallic compounds,\textsuperscript{14} prolonged reduction and nitridation of metal precursor complexes, plasma synthesis,\textsuperscript{15} self-propagating high-temperature synthesis,\textsuperscript{16} and so on.

Recently, the use of microwaves has been found to offer several advantages for the synthesis of many inorganic materials as compared to conventional methods.\textsuperscript{17-20} The foremost of these advantages are the very short time periods involved in the synthesis, enhanced reaction kinetics, and the reactant selectivity during energy transfer from the microwave field.\textsuperscript{21} Furthermore, the high reaction rates during microwave irradiation open up the possibility of retaining the nanostructures from nanopowders after processing and the possibility of synthesizing meta-stable high-temperature phases.\textsuperscript{22} Contrary to the preparation of oxide materials, only very few reports are available on the microwave-assisted synthesis of nitrides.\textsuperscript{23-22} These reported microwave-assisted nitridation reactions involving oxide precursors suffer from the requirement of relatively longer time duration (several hours)\textsuperscript{23} and often result in incomplete nitridation leading to oxygen impurities. The carbothermal route often requires an additional air-roasting step to remove excess carbon.\textsuperscript{26} In the conventional nitridation of a
metal compact, the surface nitridation precedes the bulk, which limits further diffusion of nitrogen into the metal. We envisioned that this reaction-limiting complication could be circumvented by the inverse temperature gradient (inside → out), a unique feature of the microwave method, leading to complete nitridation of the metal. Thus, in our continuing efforts to accelerate selected chemical reactions and simplify synthetic procedures using microwave irradiation, 27–30 we have developed a novel, simple, and fast metal nitridation procedure for the preparation of a number of technologically important nitrides by microwave-assisted combustion. The present method, involving the combustion reaction of a porous metal powder compact with high-purity N₂ in the microwave field, appears to be quite general for the synthesis of nitrides and yields products of good crystallinity, structural uniformity, and excellent phase purity.

II. EXPERIMENTAL

The schematic diagram of the microwave setup used for the nitridation experiments is depicted in Fig. 1. The setup consists of a modified commercial microwave oven producing microwaves at 2.45 GHz (Amana Radarange®) and capable of using various reactive/inert atmospheres and obtaining temperatures up to 1600 °C. High-purity metal powders of Ti (99.99%: −325 mesh; A.D. Mackay, Inc., New York, NY), V (99.9%: −325 mesh; Aldrich Chemical Co., Milwaukee, WI), and Al (99.9%: −325 mesh; Alfa Aesar, Ward Hill, MA) were used. The required metal powder was mixed thoroughly with NH₄Cl (J.T. Baker Chemical Co., Phillipsburg, NJ) in a 1:1 weight ratio in an agate mortar and pestle. The powder mixtures were cold pressed (using a Carver laboratory press) at various compaction pressures from 75 to 300 MPa, without using any binder. The diameter of the pellets was 1.25 cm. The sample pellet (weighing around 1–3 gms) was loaded inside a 2-inch-long mullite tube coated (on the outside) with an indigenously developed microwave-absorbing carbon paste. 31 The coated tube was housed inside a long mullite tube (which runs through the microwave cavity) with appropriate thermal insulation. The coating is used here only as a secondary heater in the microwave field and provides a hybrid-heating situation. It should be noted that the metal powders could also independently couple with microwaves to attain elevated temperatures due to eddy currents generated in small metal particles. 32–34 This combined effect produces a more uniform heating of the metal compact. All the metal nitridation reactions were performed in flowing N₂ gas (purity 99.999%; O₂ < 10 ppm) atmosphere with a flow rate of 500 ml/min. The reaction was started by switching on the microwave oven and the maximum power used was about 800 W. The temperature of the sample was monitored using a dual wavelength pyrometer (from Mikron Instruments Co., Inc., NJ). It was found that the sublimation of NH₄Cl starts around 400 °C and completes in 40–50 s after reaching this temperature (which can be monitored by the appearance and disappearance of the white smoke from the pellet). This results in a porous pellet and the flowing N₂ gas fills the generated voids inside. Then the sample gets ignited and a complete combustion reaction (between the metal and the trapped/flowing nitrogen gas) occurs. By visual examination it appears that the ignition starts at the center of the pellet and moves outward, resulting in complete combustion. The ignition temperature (Tₘ), ignition time (tᵢ), and the combustion temperature (T₄₀) were found to differ for different metals. Tᵢ and T₄₀ were also found to vary as a function of compaction pressure (green density). The microwaves were switched off once the combustion reaction was completed. A porous combustion product resulted in all the cases and the pellets did not lose their shape, indicating no melting of the metals. The products were easily crushable and were ground and characterized by powder X-ray diffraction (XRD) (PAD S, Scintag, Inc., CA), scanning electron microscopy (Hitachi S-3500N scanning electron microscope integrated with X-ray microanalysis system), energy dispersive X-ray spectroscopy (EDS), thermogravimetric analysis (Universal Thermal Analysis Instruments; the experiments were conducted in air at a heating rate of 10 °C/min), and infrared spectroscopy (Magna-IR-560 spectrometer from Nicolet Instruments Corp., Madison, WI; the measurements were carried out on thin specimen disks made using a mixture of KBr and the microwave-prepared nitride powder).
III. RESULTS AND DISCUSSION

As mentioned in the experimental section, NH₂Cl completely sublimes from the reaction compact, leaving a porous metal compact filled with N₂ gas. Once the ignition temperature is reached, the metal compact gets ignited and the combustion reaction between metal powder and N₂ gas ensues. The maximum microwave power used was only 800 W. It is interesting to note here that in the case of conventional combustion reactions where resistive heating is used to ignite the metal compact, it was necessary to apply at least 1600 W power (on a tungsten filament) to initiate the reaction. At lower power levels no ignition was observed. Also, in the conventional process the combustion starts at the surface of the pellet and propagates inwards. It is possible that since a more uniform volumetric heating takes place in the microwave process, the ignition could be achieved at a much lower power level in the present situation. It is also possible that the ignition temperatures might have been brought down in a microwave-assisted process. Indeed, there are many reports that favor a reduction in both processing temperature and time in a microwave procedure compared to conventional processing. The presence of NH₂Cl (used as a parting agent) in the reaction mixture successfully prevents the coalescence of the metal particles prior to nitridation. Once it sublimes, the generated voids are filled with flowing N₂, ensuring an adequate supply of nitrogen throughout the reaction compact. The present microwave-assisted procedure also ensures a complete combustion, resulting in no unreacted metallic phases, leading to nearly 100% product yield. However, conventional combustion synthesis of AlN, for example, leaves behind almost 10% of the unreacted metallic Al (this necessitates a postsynthesis purification step).

Figure 2 give the x-ray diffractograms of the microwave-prepared metal nitrides. The good crystallinity and phase purity is quite evident. No residual unreacted phases were detected. The calculated lattice parameters match well with the reported values (Table 1). Typical time–temperature (t–T) profiles for the microwave-assisted synthesis of nitrides are given in Fig. 3. The ignition temperature and combustion temperature of the reactions vary with respect to the metal involved, and these values are listed in Table 1. From Fig. 3, it is clear that the AlN reaction compact reaches a much higher temperature than the TiN compact. This could be due to the fact that the reaction enthalpy for the formation of AlN (−418.4 kJ/mol) is higher than that for TiN formation (−336 kJ/mol). Also, the high thermal conductivity of Al (and that of the product AlN) might be helpful for the dissipation of thermal energy from the reaction compact. And, hence, AlN compact requires a greater ignition time. It is found that the ignition time (t₀) decreases in the order TiN < VN < AlN for the same compaction pressure, suggesting that the microwave-absorbing ability of Ti powder is better than that of V, which in turn is better than that of Al. This also agrees with the earlier observations on the microwave susceptibilities of different elemental powders.

![Figure 2](image)

**FIG. 2.** X-ray diffractograms of the metal nitrides prepared by microwave-assisted combustion.

![Figure 3](image)

**FIG. 3.** Time-temperature profiles for the microwave synthesis of nitrides.

| TABLE 1. Preparative conditions for the microwave-assisted synthesis and the lattice parameters of the prepared nitrides. |
|-----------------|-----------------|-----------------|
| Compound        | T₀ (°C)         | Tₚ (°C)         | Lattice parameters (Å) |
| TiN             | 574             | 968             | α = 4.243 (4.242) |
| VN              | 830             | 1432            | α = 4.131 (4.139) |
| AlN             | 1002            | 1440            | α = 3.100 (3.111) |
| GaN             | ...             | ...             | α = 4.999 (4.979) |
|                 | ...             | ...             | c = 5.900 (5.178) |

GaN is synthesized using Ga₂O₃ and ammonia gas without involving a combustion.

*Literature values are given in parentheses.*
The effect of compaction pressure on the ignition temperature and combustion temperature for the microwave-assisted synthesis of TiN is depicted in Fig. 4. Both $T_{ig}$ and $T_{comb}$ increase with increasing pressure. Pellets with lower green density (more porous) ignite and combust more easily. The combustion is also facilitated by the availability of more N$_2$ in highly porous pellets (having more free volume). More trapped nitrogen provides better thermal insulation and allows the heat to be contained within the pellet, thus promoting ignition. At higher densities, increased metal particle contact favors the heat dissipation from the pellet, and, hence, $T_{ig}$ increases.

As mentioned earlier, in the conventional nitridation process the reaction starts at the surface and proceeds inward. In fact, during the conventional combustion synthesis of AlN, two different exothermic reaction stages were reported: the first one (at 1227 °C) corresponds to the formation of AlN particles at the surface, and the second one (at 1927 °C) corresponds to the formation of AlN fibers at the center of the compact. The microstructural studies in that case indeed revealed the presence of AlN fibers only at the center region of the reaction compact. In contrast to this, the present microwave-assisted hybrid-heating procedure provides only a single-step combustion process (see the i-T profile for AlN) involving a uniform bulk nucleation. This is further evidenced by the fact that we observed the presence of AlN fibers throughout the reaction pellet, that is, at the surface, center region, and at the bottom portions (see the scanning electron micrographs [Figs. 5(a), 5(b), and 6(a)–6(c)] of the AlN pellet viewed from the surface and at various cross-sectional positions). The fiber thickness is about 0.1 to 0.2 μm and the length varied between 20 to 40 μm. Apart from the fibers, single crystalline whiskers of AlN with a clear faceted hexagonal morphology were also seen at some portions of the reaction compact. This clearly indicates the uniform heating of the reaction compact and the availability of the reactive nitrogen gas at all portions of the pellet (due to its porous nature). This also reveals that one can achieve structural uniformity of the product using the present microwave procedure.

**FIG. 4.** Variation of ignition temperature ($T_{ig}$) and combustion temperature ($T_{comb}$) with respect to compaction pressure for TiN synthesis. The green densities of the pellets are $\rho_1 = 1.87$ g/cc, $\rho_2 = 1.94$ g/cc, and $\rho_3 = 2.00$ g/cc.

**FIG. 5.** Scanning electron micrographs of the AlN pellet, giving views of the (a) top surface and (b) bottom surface.
clear from the spectra that there is no oxygen contamination in the prepared nitrides (see the expanded version of the nitrogen spectral line; there was no detectable oxygen edge observed). The spot analysis at different nitride particles revealed the same composition, indicating the compositional homogeneity of the samples.

The stoichiometry of the microwave-prepared nitrides was also confirmed using thermogravimetric analysis (TGA) (Fig. 9). The TGA results provide the oxidizing ability of the nitride powders and their thermal stability in ambient air. The extent of oxidation (weight gain) gives a clear indication of the stoichiometry of the nitride product. For example, TiN shows a mass gain of 29.02%, which is very close to the theoretical value of 29.06% (expected for the oxidation of TiN to TiO₂).³⁴ confirming that the product obtained by the microwave method is stoichiometric TiN. The vanadium nitride is found to exhibit a multistep oxidation process and again the total weight gain is in the expected range for complete sto-
chiometry). The microwave-prepared AlN is found to be thermally stable up to 800 °C with only very little weight gain. There was no significant weight gain observed between 450 to 500 °C, which is a characteristic oxidation temperature region of metallic Al. This confirms the complete nitridation achieved during the combustion reaction (without leaving any residual elemental aluminum).

Figure 10 gives the typical infrared (IR) spectrum obtained for the microwave-prepared aluminum nitride. The IR spectrum exhibits a strong but broad absorption band in the range 400–1100 cm⁻¹ with a maximum at 685 cm⁻¹. This corresponds to the –Al–N– stretching vibrational frequency in the wurtzite structure. None of the characteristic peaks corresponding to Al₂O₃ are seen, indicating the chemical purity of the microwave-synthesized sample.

Employing the microwave-assisted procedure, nitrides of Cr, Nb, and Ta were also prepared using the mixture of the respective metal powders Cr, Nb, Ta, and NH₄Cl. However, the exact mechanism of the microwave-assisted metal nitridation reactions is still unclear. Since in no cases have we observed melting of the metals involved, the reaction appears to be directly microwave activated at the metal-particle surface in contact with nitrogen. The eddy currents generated in small metal particles in the microwave field combined with the microwave-absorbing ability of the carbon coating provide a more uniform heating of the metal compact, which ensures a complete single-step nitridation. Effective utilization of the reaction enthalpy of the 2M (metal)

FIG. 9. TGA thermograms of the microwave-synthesized nitride samples AlN, TiN, and VN.

FIG. 10. Infrared spectrum of microwave-prepared AlN.
+ $N_2 \leftrightarrow 2MN$ reactions could also be helpful in escalating the reaction rates. The rotational modes of $N_2$ may also be excited in microwaves and help nitridation.

As a limitation, the present metal nitridation procedure was not found to be directly adaptable for the preparation of GaN. It was found difficult to handle liquid metal Ga in the microwave cavity; in this case, once the sublimation of NH$_4$Cl is completed, the pellet loses its shape and forms a blob of liquid Ga. However, when high-purity Ga$_2$O$_3$ (99.999% from Alfa Aesar, MA) was used in place of Ga metal and mixed with NH$_4$Cl (in a 1:1 weight ratio and pelleted at 157 MPa), formation of GaN was successfully achieved. In this case, flowing anhydrous ammonia was used as a reductant as well as a reactant gas. After the sublimation of NH$_4$Cl, the pores of the reaction compact get filled with ammonia gas. Though no combustion was observed, phase-pure GaN product resulted after a soaking time of 20 min at 950°C. Figure 11 shows the powder x-ray diffractogram of the microwave-prepared GaN. All the peak positions and the calculated lattice parameters are found to match well with the reported values (Joint Committee on Powder Diffraction Standards card No. 2-1078). It is interesting to note here that the use of ammonia for the reduction cum nitridation reactions in the microwave field increases the reaction rates several fold when compared with the use of gaseous mixtures of N$_2$ and H$_2$. While the plasma nitridation of Ga$_2$O$_3$ using N$_2$/H$_2$ mixture in the microwave field is found to require several hours of heating for the complete formation of GaN, the use of ammonia provides phase-pure GaN in just 20 min. It may be possible that NH$_3$ couples with the microwave field through its rotational modes and forms species like NH$_3^-$ (amide) and NH$_2^-$ (imide) in the plasma state. This increases the electron density on nitrogen and can facilitate a more favorable attachment of nitrogen to Ga$^+$ ions, leading to rapid formation of GaN.

IV. CONCLUSIONS

The microwave-assisted combustion method is demonstrated to be a simple, rapid, and attractive procedure for the synthesis of a number of technologically important metal nitrides. The microwave products were found to possess excellent crystallinity and phase purity. When suitably modified, the method can also be extended for the preparation of metal nitrides from their respective oxides.

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